THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

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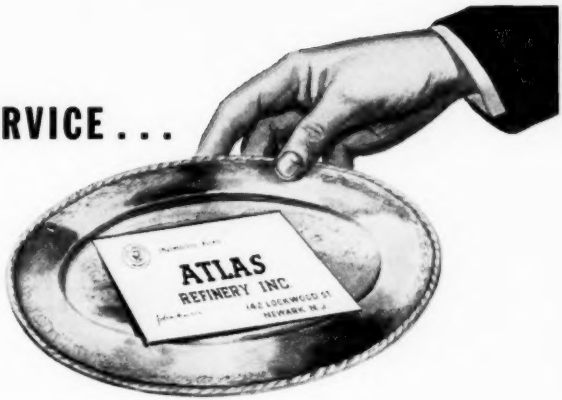

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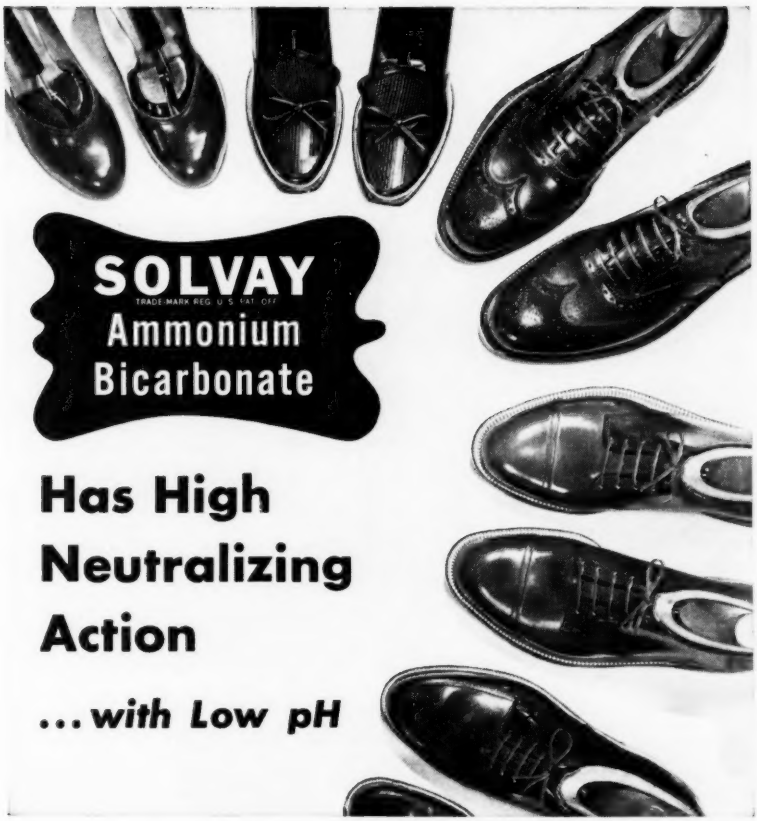

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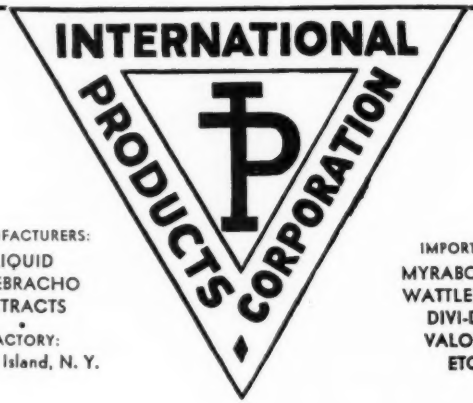

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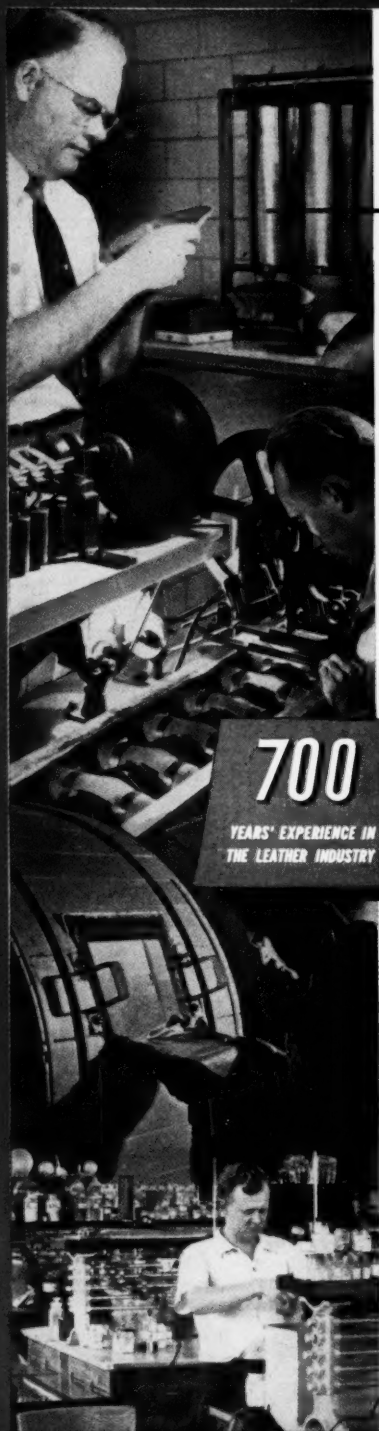

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Water of crystallization	35% Min.

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Mol. Wt. 56.1
M.P. . . . . 55°C

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ANALYSIS

NaSH	70 to 72%
Na_2S	2.5% Max.
NaCl	0.8% Max.
Na_2SO_3 and $NaHCO_3$	0.4% Max.
Fe	5 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	28 to 26%

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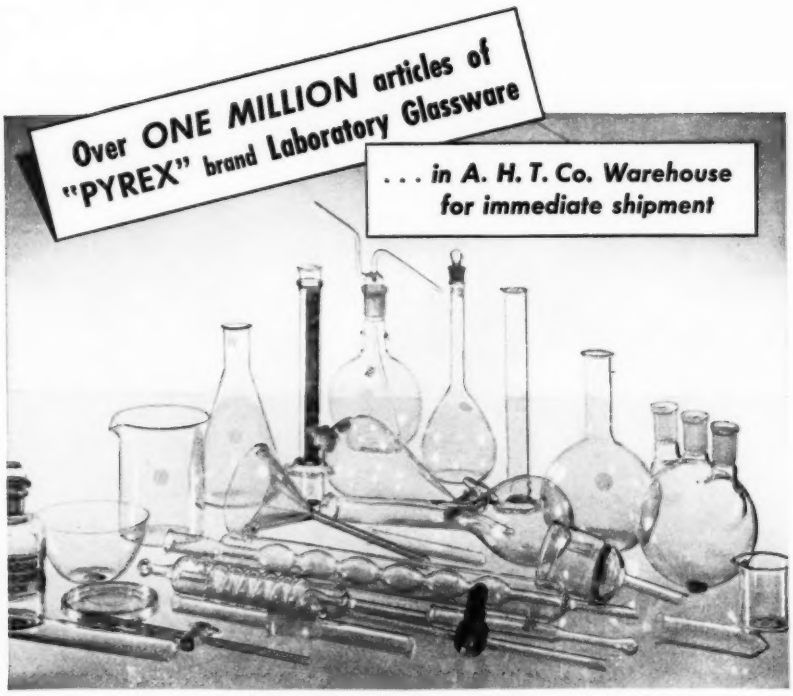

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VOL. XLVIII SEPTEMBER 1953 No. 9

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ALPHONS OTTO JAEGER

Alphons Otto Jaeger of the American Cyanamid Company died suddenly on July 21st at the age of 67. After coming to this country in 1923, Dr. Jaeger was associated with the National Aniline and Chemical Company, the Seldon Company and the parent company, the American Cyanamid. He retired in 1951 but continued as consultant for his company. He became an active member of our Association in 1933. Dr. Jaeger held many patents in both the organic and inorganic fields. He is survived by his wife and four children.

MINUTES OF MEETING OF THE SUPERVISORY COMMITTEE ON TANNING ANALYSIS

JUNE 7, 1953

Netherlands Plaza Hotel
Cincinnati, Ohio

The meeting convened at 10:00 A. M. Those present were Chairman, A. N. Kay, I. D. Clarke, C. W. Beebe, John M. Seltzer, G. V. Downing, J. M. Hinkle, L. Sheard, Allan Lauder, Joe Jany, Martin Baum, R. L. Young, Jr., F. F. Marshall, C. W. Mann, L. M. Whitmore, Craig Blair, J. S. Rogers, E. L. Rayfield, T. C. Blair, E. S. Flinn, R. B. Hobbs, J. R. Kanagy, J. F. Wagoner, C. G. Telander, R. M. Lollar and Gene Stanbery.

The purpose of the meeting was to discuss new work to be considered by the Committee as well as working out the final details of the revision of the Official Tannin Analysis Methods.

Request was made for a qualitative and quantitative method of detection and estimation of Lignosulfonates in tanning materials. After a discussion of a number of possible methods, Mr. Kay appointed Messrs. Jany and Wolfe to head a sub-committee. The following volunteered to assist: Messrs. Kanagy, Rayfield, Baum, Hinkle, and Miss V. R. Power.

Second subject for discussion was whether drying time for residues should be fixed. Much comment was made on differences in Hide Powder Committee results on total solids, soluble solids and non-tannin. It was pointed out by Dr. Flinn that the only function of the Hide Powder Committee is to test non-tannins given by new and old hide powder lots, but it was agreed that a study of all available data should be useful. Dr. Lollar agreed to work out a scheme for comparative analysis, if given the number of variables to be considered, to assist Mr. Craig Blair in formulating some committee work to determine limits for total solids residues. It was agreed, however, that data submitted by Wagoner, Kay and Blair was sufficient to warrant setting the drying time for residues at 17 hours $\pm$ 1 hour.

Discussion was had on the European use of vacuum ovens for drying tannin residues as well as the use of silver and stainless steel drying dishes. No action was taken.

Mr. Sheard favored 24°C. as the temperature for cooling and filtering tannin solutions rather than 23–25°. No action was taken.

The methods for determining Iron and Copper in tannin extract and liquors were next considered. The method for determining Iron was proposed for adoption as read. There was some dissatisfaction with the Xanthate method for Copper as now in use but the Committee finally voted to make it provisional and a request be made to turn the problem over to Dr. Lollar's Committee on Modernization.

Meeting was adjourned until 4:40 P. M. Next items to consider were a number of Editorial changes in the Revised Methods for Tannin Analysis. Style of paragraphing various methods as discussed and approved.

Dr. Flinn, of the Editorial Board, asked to have the Committees' views on whether the total solids, soluble solids and non-tannin determination should be written as three methods or grouped as one. It being the final decision of the Committee to keep three methods rather than one. The Editorial Board was asked to submit their final draft of the methods for tannin analysis to the Committee for approval.

There being no further business the meeting adjourned.

GENE W. STANBERY, Acting Secretary.

THE FIFTIETH ANNUAL MEETING

This year marked the Golden Anniversary of the Association, and it was indeed fitting that the Annual Meeting was planned as a celebration of the event. The Meeting throughout reflected the painstaking efforts of the Convention Committee and the president and secretary of the Association. The ladies' program was under the able direction of Mrs. Boss. Member registration was 308; total registration was 389. Wives and guests brought the total attendance to well over 500.

Committee meetings were held in the afternoon of June 7. In the early years of the Association, committee work constituted the principal activity of the organization and consequently a major portion of the time was given over to presentation and discussion of the reports of the committees. While committee work continues to be an important activity of our organization, Association functions have expanded in keeping with organizational growth so that the convention of today reflects this varied character.

Following the committee meetings, a reception for members and guests was held. This afforded an opportunity for one to get acquainted with new attendants, and to greet old friends.

The Convention began its scheduled program on June 8, with an address by President Turley.

THE PRESIDENT'S ADDRESS

By H. G. TURLEY

The meeting will please come to order.

The Officers of the American Leather Chemists Association welcome you this morning to our Golden Anniversary Meeting in the City of Cincinnati. The Association has now reached the half-century mark. We are all proud of our membership in a society of national status representing the chemists of the leather industry. The membership has now reached over 800 members, not including the mutual members of the foreign societies. We are particularly pleased with our membership from the countries of South America, and you will be happy to know that a few members are present.

This occasion also marks the Thirtieth Anniversary of the opening of the Tanners' Council Research Laboratory at the University of Cincinnati. The ALCA last visited the Laboratory 25 years ago. We hope all members, and particularly our younger members, will take this opportunity of visiting the official research institute of the leather industry in the United States. You may not have the opportunity in the usual course of your work to visit the research staff and to see the experimental equipment provided for leather research. Through the kindness of the Tanners' Council lunch will be provided in the University cafeteria and the Meeting will adjourn to an adjacent lecture hall for the final session of the program.

During the past year, the Association has lost several members who have passed on, and I mention the names of Thomas Blackadder, Walter Buethe, Sedgwick Kistler, Carl Simon, Edwin R. Theis and H. Webster Thomas. Let us pause for a few moments of silence out of respect to the memory of our former members and friends.

Now we must welcome our new members—85 this year—and congratulate them on joining our Association. May I urge the new members to take an active part by serving on our technical committees and, in time, offering yourselves as candidates for officers of the Association.

The program this year has had the most earnest consideration by your Council and Convention Committee who felt that the program should fit the unusual occasion. We agreed that we should pay our respects to the past, acknowledge the present, and salute the future of leather technology.

Therefore, part of the program consists of a Symposium describing fifty years of progress in leather making, arranged to appeal to the practical tanners by having lectures by practical men well known in the industry, and, in a similar fashion, another part covering the chemical developments, with

talks delivered by outstanding chemists in their particular field of leather technology.

Considering the present, we shall bring to you talks on original scientific research by outstanding authorities on proteins. Dr. Linus Pauling who is brilliantly adding to our knowledge of protein structure—a topic of paramount importance in our field of leather which, as we know, concerns the conversion of protein fibers—will lecture to you and there will be other papers dealing with new aspects of collagen.

Concerning the future, the last session of the meeting will be given over to a discussion and lectures on the unique value of leather, and why leather is the natural product of choice for many articles of clothing. Dr. H. Phillips, Director of the British Leather Manufacturers' Research Association, will describe why leather is different from, and superior to, artificial fabrics. Dr. L. Edward Gaul will consider the importance of correct foot covering for maintaining the proper health and comfort of the individual. To describe one of the scientific leather training schools in Europe, we shall have Prof. P. Chambard, Director of l'Ecole Francaise de Tannerie in Lyon. This School has recently moved to new and spacious quarters. Dr. Karl Gustavson, Director of the Swedish Tanners Research Insitute, will present some original research on chrome tanning.

This part of the program was possible to carry out because Council voted to spend money from the convention fund, and especially because of the kind donations of firms who wish to remain anonymous. On your behalf, we publicly express our grateful thanks to those anonymous donors for providing the funds whereby our distinguished guests could travel to be with us,

We must mention the active part played by the Tanners' Council and the new Leather Industries of America in promoting public interest in leather in the City of Cincinnati at this time. We are glad to make available this convention as a centre for leather publicity and we hope you will take the opportunity to be of assistance in your respective capacities to the representatives of the Leather Industries of America.

As chemists, we owe a debt to these trade organizations who promote the use of leather in which we gain our livelihood. In turn, we can help in a scientific way to provide results and ideas for keeping leather before the public. Last year your president, Dr. R. Koppenhoefer, organized a Leather Industry Advisory Committee under the chairmanship of Mr. Charles Morrison, a Council member, and two meetings with Mr. W. Kraus, Director, and the staff of L. I. A. have been held, and the foundation has been laid for future cooperation in guiding the flow of technical information and providing new sources of information and new ideas. I hope you all read and have taken to heart the request in Mr. Kraus' letter in the April issue of the Journal and will send in your ideas. What helps L.I. A. helps us and our Association.

In recent years, the leather industry has been challenged by new industries producing synthetic materials, and they have made progress in some limited directions. Now our industry is fighting back to maintain and improve our position by using modern techniques of advertising in magazines, newspapers, radio and television. The results so far are most encouraging and our efforts have only just begun. Other basic, staple industries have been aroused by the inroads of substitutes and have taken on a new lease of life and are making recoveries. I think I can give voice to your sentiments when I say we shall welcome competition from satisfactory, acceptable substitutes, but we shall fight back and fight hard with all the resources of our Technology, Science, and Imagination. However, we most assuredly will not accept competition from poorly made, poorly performing, unacceptable synthetic products no matter from where derived or however promoted.

We now turn to the business affairs of the Association. Considering first the finances of the Association—the balance sheet for 1952 has just been published in the current Journal–page 279. I am happy to say we operated at a profit. The excess of income over liabilities amounted to $4,718.36—a slight decrease of $374.74 over 1951. This was on a total income of $31,947.57. The Journal income of $19,348.49 is slightly less than the Journal expenses of $20,081.45 by a margin of $432.96 or about 3½% of the cost of operation of the Journal. This we consider as marginal and can be improved by a slight increase in the amount of advertising income or a few pages less of printed matter in the Journal. However, in principle we always accept scientific contributions in toto—for the Journal. Our proposed budget for 1953 is set out on page 271. We allowed for slightly reduced receipts from the sale of Journals and reprints, and budgeted more for printing the directory and for the annual meeting. We expect a slight increase in dues from a gain in membership.

Our surplus continues to increase and has reached a sum of $46,981.19. We regard this accumulation of surplus funds—on the advice of the Chairman of the Ways and Means Committee, Mr. J. Teas—as a sound policy to safeguard against the contingency of a lowered income due to loss of membership if we find ourselves in a period of national or world-wide economic depression. However, as a non-profit organization we must consider also the growth of our reserve funds. We welcome suggestions from members—it is your money—as to suitable disbursements which, at the same time, would safeguard the financial structure and preserve the integrity of the Association.

Our technical committees have been active. No committees have been discharged this year. A new committee—the Mechanical Leathers Committee—under Mr. A. S. Berens has been organized and has had one meeting. The President-Elect, Dr. E. S. Flinn, as Coordinator, will make a report to Council on the status of the committee work.

The revision of methods leading to the new Methods Book has been seriously studied for the past three years. I am glad to say we have made a start. Mr. Maeser's committee on Physical Testing has worked very hard, and the first results appeared in the April issue of the current volume of the Journal, as a revision of the Physical Methods and 26 methods were described. There have been material changes in most methods so that under the By-Laws these methods must revert back to provisional status and this was so recommended by the committee.

In presenting the methods for the Methods Book, there have been some honest differences of opinion as to a suitable system of numbering and identifying the methods. One group favors a simple system for ready reference, while another group favors the system adopted by the Federal Specifications Board. The methods previously referred to in the April issue of the Journal have been numbered on the simple system. To settle this point, Dr. E. S. Flinn is meeting with the Chairmen of the committees concerned and hopes to arrive at a final decision during this meeting. I would ask those chemists who use these methods frequently to write your suggestions and criticisms from time to time to the Technical Coordinator or your Secretary, because it is the aim of our Association to have the very best methods which shall be of the greatest value to our members.

The important question of the supply of Standard Hide Powder was resolved this year. After much debate and legal advice, it was agreed that the manufacture and supply of hide powder was a commercial venture that did not come within the province of the Association, and so the matter of an option on the manufacture of hide powder was dropped as being of no concern to the ALCA. The Hide Powder Committee still, as in the past, tests and certifies the new batches of hide powder as made available by the manufacturer.

In conclusion, I wish to record our appreciation of the services rendered during the past year by our President-Elect in compiling the methods for printing—a painstaking job of fine detail; your various committee chairmen, particularly Mr. Kay of the Tannin Analysis Committee—a laborious job of manipulating detail; and Mr. Telander of the Federal Specifications Committee who has constantly safeguarded the interests of the industry; the Editor of the Journal and the office of the Secretary, with a word of praise for Miss V. Becker, our Executive Secretary.

June 8, 1953 H. G. TURLEY.

A short business session followed. Papers were then presented in the following order:

Morning Session—June 8

UNI- AND MULTI-POINT BINDING OF CHROMIUM COMPLEXES BY COLLAGEN AND THE PROBLEM OF CROSS-LINKING

by K. H. GUSTAVSON

MODERN PRACTICES IN TWO BATH CHROME TANNING
by E. E. Ochs

EFFECT OF SPLITTING ON BREAKING LOAD AND TENSILE STRENGTH OF GRAIN AND CORIUM SPLITS FROM CHROME TANNED LEATHER.
by M. Maeser

EXTRACTION METHOD FOR DETERMINATION OF ORGANIC ACIDS IN VEGETABLE TANNING LIQUORS
by H. H. Silvestra and C. G. Telander

Afternoon Session—June 8

RECENT ADVANCES IN THE KNOWLEDGE ABOUT THE STRUCTURE OF PROTEINS
by L. C. Pauling

SWELLING OF COLLAGEN AND MODIFIED COLLAGENS
by J. Cassel and E. McKenna

HEATS OF WETTING COLLAGEN, LEATHER AND OTHER ORGANIC AND FIBROUS MATERIALS
by J. R. Kanagy

ELUCIDATION OF TANNING MECHANISMS
by E. R. Theis and R. L. Stubbings

TANNIN ANALYSIS METHOD—PROBLEMS AND MODIFICATIONS
by M. Baum, R. C. Camp and J. R. Salvesen

Morning Session—June 9

This day was devoted to a Symposium on Fifty Years of Leather Making. In the morning, practical papers were presented as follows:

THE AMERICAN LEATHER CHEMISTS ASSOCIATION
by H. G. Turley

SOLE LEATHER
by L. M. Whitmore

SHOE LEATHER
by B. D. EISENDRATH

DYEING LEATHER
by R. LEACH

LEATHER OILS
by T. A. Faust

LEATHER FINISHES
by A. J. PILAR, SR.

TANNING MACHINERY
by T. C. HOLLANDER

The afternoon session opened with the presentation of a paper on the

FRENCH TANNING SCHOOL AND LEATHER RESEARCH INSTITUTE
by PROFESSOR PAUL CHAMBARD

Papers were given on the chemical nature of leather making. They were presented as follows:

COLLAGEN STRUCTURE
by J. H. HIGHBERGER

STRUCTURE OF VEGETABLE TANS
by R. M. LOLLAR

THE DEVELOPMENT OF SYNTANS IN THE U. S. A.
by R. BLACKADDER and I. C. SOMERVILLE

LEATHER DYESTUFFS
by C. K. BLACK and G. H. GEISTER

The Golden Anniversary Banquet was held in the evening. A report of the evening's activities appears elsewhere in this Journal. It is sufficient to note that the Moffat Medal, the Alsop Award, the Winheim Award, and Life Membership presentations were made at the banquet.

Morning Session—June 10

Visit to the Tanners' Council Research Laboratory.
Luncheon courtesy Tanners' Council of America.

Afternoon Session

Papers were presented as follows:

WHY LEATHER FOR FOOTWEAR AND CLOTHING
by H. PHILLIPS

SHOES AND FOOT HEALTH
by L. E. GAUL

CANAIGRE ROOT TANNIN MAKES SERVICEABLE LEATHER
by C. W. BEEBE, W. S. KIP, W. F. HAPPICH and J. S. ROGERS

REACTIONS OF VEGETABLE TANNED LEATHER II
by S. S. KREMEN, B. L. LUCAS and R. L. SOUTHWOOD

The Convention was indeed honored by the attendance of K. H. Gustavson, Director of the Tanning Research Institute of Stockholm, Sweden; Linus C. Pauling, Professor of Chemistry of the University of California; Professor Paul Chambard of the French Tanning School and Leather Research Institute; and H. Phillips, Director of the British Leather Manufacturers Research Association. At no time in its past history has an A.L.C.A. Convention been privileged to have present so many men who are prominent in their chosen fields.

During the afternoon of June 10th, the Annual Golf Tournament was held. This crowded the schedule somewhat, but did not mar the pleasure of the game for the participants.

The principal awards were as follows:

TEAS MEMORIAL CUP–Low Gross–JIM MORRISON.

SENIOR CUP–Low Gross–Active–RICHARD DREW.

L. A. CUTHBERT MEMORIAL CUP–Low Net–Active–A. H. STUEWE.

REILLY-WHITEMAN-WALTON MEMORIAL CUP–Low Net–Open F. P. MACKINNEY.

The tellers announced the election of Council Members as follows:

R. G. HENRICH J. R. KANAGY H. R. WILSON

GOLDEN ANNIVERSARY BANQUET CEREMONY

Acceptance of Testimonials and Presentation of Awards

Dr. H. G. Turley

Ladies and Gentlemen: I would not wish to impose on your enjoyment of your banquet but we have now arrived at a serious point in our Golden Anniversay celebration. This is the moment when we acknowledge the greetings and well wishes of our sister societies and of the eminent leather scientists of the world. Also, the outstanding honors of the leather industry and of the Association are being awarded tonight to some of our distinguished members.

First, you will be happy to know that we have received congratulations from our national parent society of all chemists—The American Chemical Society. I would like to read you a letter received from Dr. Farrington Daniels, the new President: "The American Chemical Society congratulates the American Leather Chemists Association on the important occasion of the 50th Anniversary of its founding. May I ask you to carry the sincere greetings of the American Chemical Society to your Jubilee meeting which is to be held in Cincinnati, Ohio, June 7 to 10. The American Chemical Society is greatly interested in sister societies which serve specialized segments of the field of chemistry and we are impressed with the record of achievement and leadership of the American Leather Chemists Association during these past fifty years. We express the wish that the coming years will lead to still greater success and service."

We have received greetings from leather chemist societies all over the world, not only in Europe but even as far away as in New Zealand, down under. Allow me to read to you the greetings from the South African Society of the Leather Trades' Chemists, from their President, Carl C. Kritzinger: "Kindly convey our very best wishes for a very successful and memorable meeting on the occasion of your Golden Anniversary Convention this year in Cincinnati. Those of our members who are also members of the American Association are proud, in this year as never before, to belong to that Association." Some of you will remember Dr. Kritzinger when he was over here studying at Lehigh University.

We received cordial messages of congratulation from the Swiss Leather Chemists Association, the Italian Leather Chemists Society and the Spanish Leather Chemists Society, among several others. I think it is quite touching that we received congratulations from the small handful of Chinese leather chemists who are still maintaining their freedom in Formosa. They write: "Please accept the warmest congratulations for your 50th Anniversary extended by the undersigned chemists in the Tanning Industry of Free China, and their best wishes for your continued success and prosperity. Your record of achievement on the promotion of the science of leather tanning for the past

half century represents not only a career of the highest scientific standard, but also one of genuine contributions to our tanning industry. You have every right to be proud of the respect, confidence and admiration you have won." May we wish them continued success in their scientific work, untroubled by political interference.

Other famous institutes have sent their congratulations. You will be particularly pleased to hear the message from Dr. Donald Burton, Head of the Leather Industries' Department at the University of Leeds, England. "I wish to send my heartiest congratulations to the American Leather Chemists Association on the occasion of their Fiftieth Anniversary, and my best wishes for the continued success of their valuable work for many years to come. The members of the staff of the Leather Industries' Department join me in these good wishes." As many of you know, Leeds was probably the first scientific center for leather technology and has influenced all leather research since the days of the distinguished Henry R. Procter.

We have congratulations from the British Boot, Shoe and Allied Trades Research Association, the New Zealand Research Association, and the French Tanning School is ably represented here this evening by Prof. Chambard. Then a message from the Institute of Pure and Applied Chemistry of Ankara, Turkey, from Prof. O. Gerngross, and finally, from the Central Leather Research Institute, Madras, India, from Dr. Y. Nayudamma who spent several years here learning leather science at Lehigh University.

We are particularly touched by messages from some of our distinguished members. I would especially like to read you a letter we received a few days ago from Mr. George Kerr, our first President fifty years ago: "Failing my presence I would like to convey to the officers, council, and members of the Association my sincere congratulations on the conspicuous success they have brought to the A.L.C.A., and also my very best wishes for a continuance of its great accomplishments." I am sure you will all be with me in sending a telegram to Mr. Kerr from this Meeting, expressing our disappointment in not having him with us and wishing him good health and happiness.

We had a letter from Prof., Stiasny the great European leather chemist; "My heartiest congratulations on behalf of the Golden Anniversary of the American Leather Chemists Association and my sincere greetings to my friends who are celebrating this day in Cincinnati." Since his old friend and associate, Dr. Gustavson, is here this evening, we shall ask him when he returns to Sweden to convey to Prof. Stiasny the sentiments of our Association and wish him good health and happiness.

We also have good wishes from Prof. Louis Meunier, the grand old man of French leather chemistry. You will remember his early researches in the 1920's and his discovery of the Quinone tannage and his fundamental work on the fish oil tannage for chamois leather.

On this occasion, your Convention Committee has worked long and arduously under the Chairman, Dr. J. S. Kirk and this Convention has been

graced by the presence of three outstanding European leather scientists. This evening I want to present to you Prof. Chambard, who is here in a dual capacity: First, as a representative of the International Union of Leather Chemists Societies. Dr. Chambard was the first President after the war and officiated at the Paris meeting in 1949. Your Society, under Mr. A. Winheim, decided to join this international group, and your delegates have been delighted with the cordial reception given them and the spirit of friendship and cooperation displayed at the international meetings. We hope this is a happy augury for the future and that these international meetings will continue on this friendly basis and the A.L.C.A. will take an active interest in their deliberations, and in a small way do our part in promoting international harmony and good will through that love of our common interest which is leather.

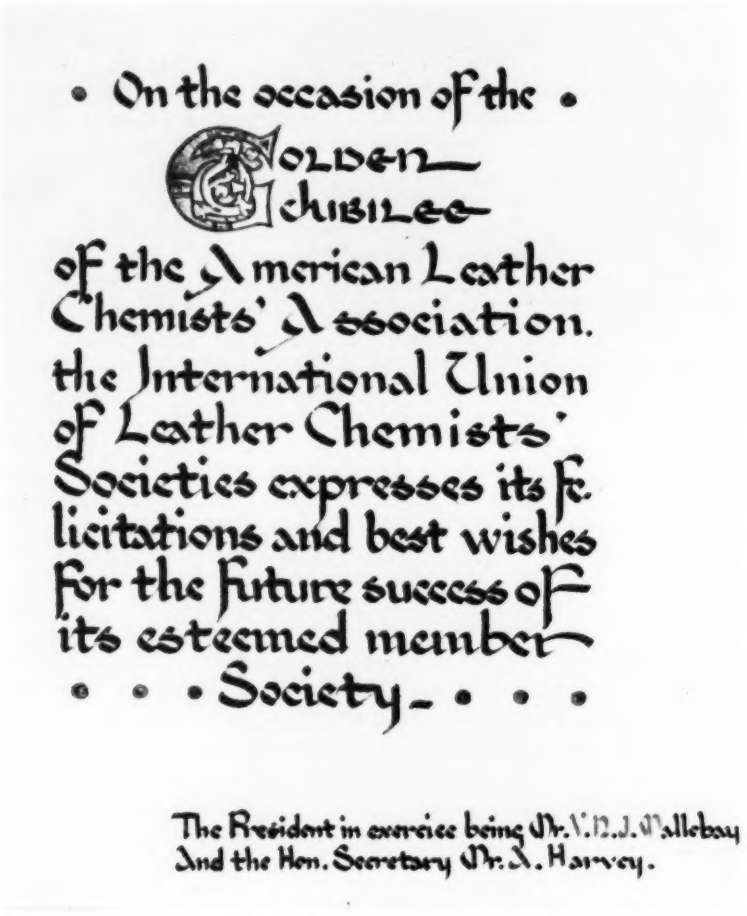
Prof. Chambard is also Director of the French Tanning School and the Institute of Leather Research. It was my good fortune to visit him in 1949 and I saw the fine new tanning school. I would urge any of you who have the opportunity, to pay them a visit while you are in Europe. Dr. Chambard has succeeded Prof. Meunier and I am sure the future of leather research and training in France are in very capable hands. Ladies and gentlemen, I present Dr. Chambard.

PROF. P. CHAMBARD

"Mr. President, Ladies and Gentlemen: You will certainly be kind enough to excuse my English, and you will permit me to present to you the felicitations of the International Union of Leather Trades' Chemists Societies. I recall that before the war we had in Europe an International Society of Leather Trades' Chemists. I was the last president of that Society. When the war ended, we tried to reorganize this International Society, but we were obliged to take notice of the completely changed economic conditions so that the old rules could no longer be observed. It was, in fact, not possible for individuals to join as members of an international organization. Therefore, it was decided to have in each country National Societies and to join together in an international federation which was named the International Union of Leather Trades' Chemists Societies. This was decided in London in nineteen hundred and forty-seven in a meeting where was present some old members of the past International Society, namely Dr. G. J. Parker, Prof. MacCandlish, Prof. Atkin, Mr. Harvey, Mr. H. Vourloud, Mr. Mallebay and myself. We framed the rules of the new organization and we invited leather chemists in different parts of the world to join us. We were extremely happy when we obtained the assurance of the American Leather Chemists Association that they would join the International Union. We thus became a really international organization. Our Union is a young one, our first conference was held in Paris in nineteen hundred and forty-nine; the second in London in nineteen fifty-one, and the third will be in Barcelona in September of this present year. We are

still a young Society but the first results are promising and we can have the certitude that the cooperation of all the leather chemists of the civilized world will have the best influence from all points of view."

"We rejoiced, Mr. President, when you so kindly invited me to attend the Golden Jubilee of your Society. The officers of the International Union charged me to bring you their felicitations inscribed on a manuscript which I beg you to accept. I will now express to you my own thanks for having invited me to attend these very interesting meetings and to be present at these splendid festivities. I beg you to accept my best wishes for the prosperity of the American Leather Chemists Association."


• On the occasion of the •
Golden
Jubilee
of the American Leather
Chemists' Association.
the International Union
of Leather Chemists'
Societies expresses its fe-
licitations and best wishes
for the future success of
its esteemed member
• • • Society • • •
The President in exercice being Mr. W. D. J. Walleboy
And the Hon. Secretary Mr. A. Harvey.

Illumined Address presented by the International Union of Leather Chemists' Societies.

DR. H. G. TURLEY

Professor Chambard, on behalf of the Association we are very happy to accept this beautiful, illuminated manuscript bearing the felicitations of the International Union of Leather Trades' Chemists Societies. We shall be proud always to display this token of your esteem and it will be preserved as a permanent exhibit in our Secretary's office."

I should now like, with particular pleasure, to introduce Dr. Henry Phillips of London. Dr. Phillips is also here in a dual capacity. He represents the Society of Leather Trades' Chemists of which he is a Council member, and he is Director of the British Leather Manufacturers' Research Association. As a young man, after a brilliant career in organic chemistry, Phillips joined the B.L.M.R.A., serving under the late Dr. Dorothy Jordon-Lloyd. Some of you will remember the visit of this distinguished former Director to this country in 1937 in which she spoke on the structure of sole leather. Phillips then spent the next years as chief scientist in the Wool Industry Research Association. Among other scientific achievements he was the inventor of a unique process for shrink-proofing woolen goods. He also made outstanding contributions to our knowledge of the chemical structure of keratins. This work was recognized by the Society of Dyers and Colourists by the award of the "Worshipful Company of Dyers Research Medal" for 1946-47.

Dr. Phillips returned as Director of the BLMRA in 1947. Dr. Phillips, therefore, brings to leather research a most unusual experience in fibre science. Naturally, his approach to problems of leather making is somewhat different and he regards leather as a specific example of fibre protein chemistry. During this Meeting he is lecturing to us on the general topic of why leather is a preferred material for footwear and clothing. His view-point is new and refreshing. I, therefore, have the greatest pleasure in presenting to you Dr. Henry Phillips, Director of the British Leather Manufacturers' Research Association.

DR. H. PHILLIPS

Mr. President, Ladies and Gentlmen: I have a very pleasant duty to perform which is to bring to you from the Society of Leather Trades' Chemists their heartiest congratulations on your attaining your Fiftieth Anniversary and to convey to you their best wishes for your future success.

May I as Director of Research of the British Leather Manufacturers Research Association also convey to you the congratulations of my British tanner members.

The Society of Leather Trades' Chemists wanted you to have a permanent momento of this occasion to mark their appreciation and recognition of the fine record and work of your Association during the last fifty years. On behalf of our President, Council and Members, I ask you Mr. President to

accept this illuminated address expressing their best wishes on this important occasion.

Might I also take this opportunity to thank your Association for your kind invitation to attend this Convention and to express my thanks to all my American friends who have conspired together to make my visit most enjoyable and profitable."

THE SOCIETY OF
LEATHER TRADES CHEMISTS

THE President, Council and Members of the Society of Leather Trades Chemists present their congratulations and their best wishes for the future to the American Leather Chemists Association on this the occasion of their Fiftieth Anniversary.

President

June 7th-10th 1953.

Hon. Treasurer. Hon. Secretary.

Ornamented Manuscript presented by the Society of Leather Trades Chemists.

DR. H. G. TURLEY

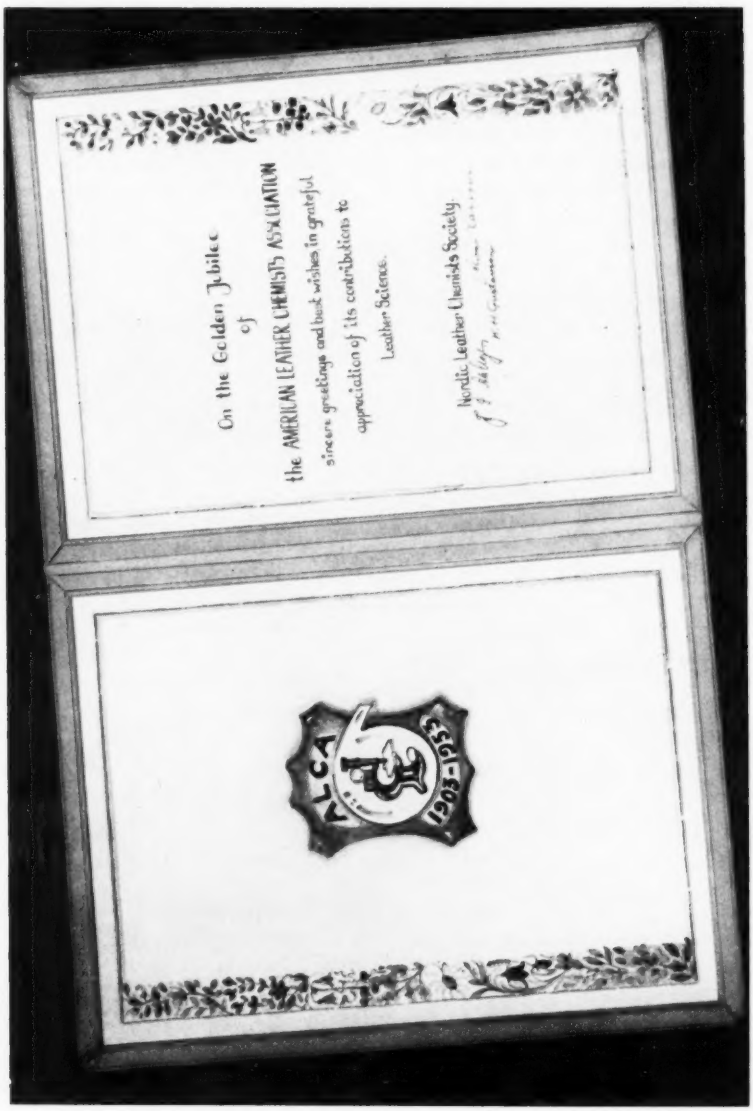
"Thank you, Dr. Phillips. Will you please convey to the President and Council of the Society of Leather Trades' Chemists the thanks of the American Leather Chemists Association for the beautiful illuminated manuscript bearing your Society's congratulations on our Fiftieth Anniversary. We shall cherish this momento of the occasion and shall ask our Secretary to have this suitably mounted and displayed in the Secretary's office for the inspection of our members and visitors.

Now, fellow Members, we present to you an old friend, well known to many of you in the past thirty years. As a young man he came to the United States from Sweden and was employed in several tanneries. He was an early contributor to our Journal and his first paper appeared in 1923, at a time when there was an impetus in leather research—the period of John Arthur Wilson, A. W. Thomas and George D. McLaughlin. Gustavson was among the first to bring to chrome tanning the knowledge of the intricacies of the chromium complexes. In 1932 Gustavson returned to his native land of Sweden and continued to enrich European scientific literature while we lost a good friend and a valued member of Council.

Gustavson has published about 125 original research papers in English, German, and Swedish as well as in our own American Journal. Most of Gustavson's work has been the amazing application of a man who hampered by a lack of assistance, in his spare time from industry or teaching, and often with reduced finances, has carried on single handedly research in the pure science of leather making. Dr. Gustavson has been invited to the United States on several occasions in recent years to give special lectures, and also to England, Germany, Spain and India. Gustavson is well known to many of our members, particularly in New England where he originally resided not as "Dr. Gustavson" but simply as "Gus". We, therefore, have the honor to present to you Dr. Karl H. Gustavson, Director of the Swedish Tanners' Research Institute."

DR. KARL H. GUSTAVSON

"It is my pleasure to represent the Nordic Leather Chemists Association and to convey to you their sincere greetings and best wishes on your celebration of the Golden Jubilee. Our Association is made up of leather chemists and technologists in the Scandinavian countries, *i. e.*, Denmark, Norway and Sweden, and Finland; with a total membership numbering 150, representing a population of 15 million people. Thus, as you see, we are a small body. Accordingly, it is not surprising to find that our resources for carrying out investigational work in our specialty are very limited, and hence, we depend to a great extent upon the results of reseaches—both fundamental and applied—which emanate from the institutions and laboratories of the more potent countries, in the first hand, the United States of America and



Leather bound Testimonal presented by the Nordic Leather Chemists Society.

ergo: your Association. We feel greatly indebted to you for your many sided activity on the various issues in our glorious field of work, more particu-

larly for the dissemination of knowledge through your outstanding Journal, which is a welcome monthly guest to a great many of our members.

The foregoing speakers, my friends Dr. Chambard and Dr. Phillips, have conveyed the greetings and best wishes of their affiliations by means of inscribed parchments. Since collagen is, after all, a versatile substance and we are leather chemists, we preferred to use crosslinked collagen in the form of leather as a carrier of our felicitations. Hence, we killed a Swedish calf, flayed it, cut a Christmas tree, carved it, and made spruce bark extract of the bark. Furthermore, we made the wood into paper by means of the sulfite process. The ensuing waste liquor became the source of the high-molecular fraction of the lignosulfonic acids. Excusing myself talking shop in the presence of a gathering sparkling with gracious ladies without collagenous aspirations, but probably applications, may I say that we made a leather of the components mentioned: in activating the cationic protein groups by the sulfo acid and imparting body to the leather by a proper tannage—hydrogen bonding is the modern word for it I believe—through the interaction of vegetable tannins by the polypeptide groups of collagen, which were readily accessible. The results of these efforts of the leather chemists and of a young lady with leather tooling as a hobby are herewith presented to you, Mr. President, in the form of this address. It reads:

"On the Golden Jubilee

of

the AMERICAN LEATHER CHEMISTS ASSOCIATION

sincere greetings and best wishes, in grateful

appreciation of its contributions to

Leather Science"

DR. H. G. TURLEY:

"Dr. Gustavson, the Association thanks you, as a representative of the Nordic Leather Chemists Association, for the lovely leather-bound illuminated address. This, I am sure, will have a special place in our affection because of the loving care and skill which went into preparing this beautiful gift. It is eminently a fine example of handcraft, possibly all too seldom seen in our age of mass production. I shall ask our Secretary to have this suitably mounted for all to see. On behalf of the American Leather Chemists Association, we convey our deep thanks and appreciation for the kind thoughts of the Nordic Leather Chemists Association on the occasion of our Golden Anniversary Meeting.

DR. H. G. TURLEY

"Ladies and Gentlemen we come now to the most important part of our whole Meeting. On this Jubilee occasion we are very pleased to announce the presentation of all the awards that the leather industry and the Association have in their power to bestow. The highest honor of the leather industry is the Fraser Muir Moffat Medal which is being presented tonight, and the Association is presenting the Alsop Award and the Winheim Award. Our Council appointed an Awards Committee of our most responsible members, under the chairmanship of Dr. W. Windus, a member of Council. We have the highest regard for the choice of this committee composed of Dr. Windus, Mr. Philip Waite and Mr. Edward Crede. I now call upon Dr. Wallace Windus, Chairman of the Awards Committee."

DR. WINDUS

"The first award is the Fraser Muir Moffat Medal. This is donated and awarded by the Foundation of The Tanners' Council. It is given for outstanding service to the leather industry. We are especially honored to have with us the president of the Foundation, Mr. Ernest Griess, to present the medal.

MR. GRIESS

"Mr. President, honored guests, members and friends of the American Leather Chemists Association; I am especially happy for the privilege of presenting the Fraser Muir Moffat Medal.

The Laboratory Foundation has since 1937 presented this medal to eight persons. The recipients were all distinguished scientists and in each instance I had to delegate some representative of the Foundation to make the presentation; it is therefore a triple pleasure for me to make the award tonight.

In this presentation I honor two men whose lives have had great influence on the Leather Industry. We honor Mr. Fraser Muir Moffat, the first president of The Tanners' Council, a man of great vision and of high idealistic principles. We honor the recipient tonight for an equal influence on the Leather Industry, although not a direct member of the Industry. I refer to Mr. Otto Haas of the Rohm and Haas Company. The accomplishments and services to the Leather Industry by Mr. Haas are well known to all and exemplify the latin motto—"Facere Non Dicere".

So in keeping with the philosophy and modesty of Mr. Otto Haas, I shall send to him, with all our best wishes, through his son, Dr. F. O. Haas, the Fraser Muir Moffat Medal with the hope that it will bring to him a happiness in the reflection that his efforts are appreciated.

Dr. Haas, please accept this medal upon behalf of your distinguished father."

Presentation of the Fraser Muir Moffatt Medal to Otto Haas by Mr. Ernest Griess. Accepted by Dr. F. O. Haas.

DR. F. O. HAAS

"Mr. Griess, Dr. Turley, honored guests, members and friends of the American Leather Chemists Association; on behalf of my father I want to thank the Tanners' Council Foundation very much for the Fraser Moffat Medal. He has told Mr. Griess that he did not feel worthy of the award, but he realizes that this is the greatest honor that has ever come to him. He told me to say that he accepts the medal in humility and gratitude not only for himself but also for the late Dr. Otto Rohm and our associates, who, at all times, have striven to be useful to the leather industry.

My father would like very much to be here to accept the Moffat Medal. However, he travels very little and restricts his activity entirely to the office. For this reason he is grateful that you have consented to let me take his place.

It was through the leather industry that we got our start in business and, therefore, leather will always be foremost in our minds. We are grateful for the assistance which the tanners have given us and in turn want to be of

help in any way that we can. Our work has been a pleasure for we are privileged to have many friends in the tanning industry.

It seems logical that the future should offer a fine opportunity for leather, for a skin is one of the most wonderful products of nature. Its complex chemical and physical structure is one which cannot be imitated by man. An increasing amount of effort is being devoted today to the chemistry of the proteins and the structure of the skin. With the assistance of the outstanding scientists working on these problems, I believe that we can look forward with confidence to future developments, for it is clear that to the general public nothing has the appeal of leather."

DR. WINDUS

"The next two awards are administered by the American Leather Chemists Association through an awards committee appointed by Council. This committee included Edward Crede of The American Hide and Leather Company, Philip Waite of A. F. Gallum and Sons and myself. I can say for the committee that it showed remarkable unanimity in its decisions.

The Alsop Award is donated by the River Plate Corporation in memory of William K. Alsop. The award is made for outstanding scientific or technical contributions to the leather industry. In regard to the suggestion on publiccations the committee gave weight to the fact that the recipient is co-author of a volume of analytical methods entitled "Analysis of Leather". This appealed to the committee as a substantial publication, whether it came in the last year or the last twenty years. Actually, there was a publication in the last three years, so the committee was able to live up to the letter, as well as the spirit of the law.

We are plivileged to have with us Mr. James M. Cavanaugh, assistant sales manager of the River Plate Corporation, to make the presentation.

MR. CAVANAUGH

"Mr. President, officers of the A.L.C.A., distinguished guests, members, Ladies and gentlemen; It is, indeed, an honor and a privilege to come before you this evening to play a small part in the presentation of the Alsop award.

I deem it only fitting, on this, the Golden Anniversary, to say a few words about the man whose memory we commemorate. Fifty years ago the Leather Chemists were a branch of the Association of Official Agricultural Chemists. Mr. Alsop played no small part in the formation of the American Leather Chemists Association as a separate entity, distinct from the old A.O.A.C. Mr. Alsop was a pioneer in the development of methods to determine tannin analysis. In 1908 he became the chief chemist of the United States Leather Company, Ridgway, Pa. His associates of that era were fully aware of his devotion to the scientific aspects of Leather Chemistry, and his exhaustive labor to disseminate that knowledge through the A.L.C.A.

Your committee this year, under the chairmanship of Dr. Wallace Windus, has selected Dr. Henry B. Merrill, as the Golden Anniversary recipient of the Alsop Award. Dr. Merrill was educated at the University of Wisconsin, graduating from the course in chemistry in 1916. He received his Ph.D. in 1921. Until 1929 Dr. Merrill worked under Mr. John Arthur Wilson at A. F. Gallum & Sons, Inc. in Milwaukee. From 1929 to 1941 he was chief chemist at Gallum's and was then called to active duty in the service of his country. Dr. Merrill served for five years in the Chemical Corps of the Army, rising to the rank of Colonel. In 1946 he succeeded the late George D. McLaughlin as Director of the B. D. Eisendrath Memorial Laboratory, which position he still holds. Dr. Merrill is author or co-author of about forty papers on various phases of leather chemistry, and co-author with Dr. Wilson on the "Analysis of Leather". He is a member of the American Chemical Society since 1921 and served as chairman of the Milwaukee Section and section-editor of the Leather and Gelatin Section of Chemica Abstracts since 1935. He has been a member of the American Leather Chemists Association since 1926, served on numerous committees and as your President 1938 to 1940. To commemorate

Acceptance of Alsop Award by Dr. H. B. Merrill Presented by Mr. James M. Cavanaugh.

this event we would like to present this little gift to Dr. Merrill. With extreme pleasure may I present to you Dr. Henry B. Merrill the Alsop Award."

DR. MERRILL

"Mr. Cavanaugh, Dr. Turley, ladies and gentlemen ever since I was told that your Awards Committee had seen fit to select me to receive this magnificent gift, I have looked forward to this presentation with much curiosity, wondering what accomplishment of mine could possibly have been considered worthy of such recognition. I still don't know. I can only conclude that your committee members have long memories, and not particularly good ones. Certainly nothing I have done in recent years is deserving of this great honor. But be that as it may, I am deeply and humbly appreciative. I shall wear this watch with gratitude, cherish it,—and try to remember to take it off before carrying out day-to-day researches in the bate paddles. Again, I thank you."

DR. WINDUS

"The last award is the Winheim award. It was established to honor the memory of Ade Winheim, who contributed substantially to the modernization of the American Leather Chemists Association.

The award is given to any full-time student of a United States educational institution for work presented or published not later than two years after graduation. The work shall be directly related to the leather industry or shall make a significant fundamental contribution to the welfare of the industry.

Since the recipient is from the leather industry's own laboratory, Dr. Fred O'Flaherty will make the presentation."

DR. O'FLAHERTY

Mr. President, honored guests, members of the American Leather Chemists Association and friends, it is with pleasure and pride that I present the 1953 Winheim Award.

It is being awarded to Dr. S. S. Kremen, presently a staff member of the Tanners' Council Research Laboratory, who as a doctorate candidate in the graduate school accomplished and published research which in the opinion of the Awards Committee has earned for Dr. Kremen the Winheim Award.

It is a pleasure to reward one for work well done, and especially when the work was accomplished without any material gain in mind. It is with pride because the work was done in the laboratory of which I have the honor to be director; and both in 1951 and 1953 the graduate work done in this Laboratory has warranted the distinction of the Winheim Award.

It is therefore with pleasure and pride that I present to you, Dr. Kremen, the 1953 Winheim Award."

Acceptance of Winheim Award by Dr. S. S. Kremen. Presented by Dr. Fred O'Flaherty.

DR. S. S. KREMEN

"Dr. O'Flaherty, Mr. President, honored guests, members and friends of the American Leather Chemists Association, please accept my most sincere thanks and appreciation for the honor that this Award represents. When I first heard that I was to receive the award, one of my first thoughts was about Ade Winheim and how all of us in this Association must miss him, both professionally and socially. If this Award serves to periodically remind us of this fact, it indeed serves a worthy purpose.

While awards are made to individuals, it should be recognized that no one works in a vacuum. A man who is studying for an advanced degree, while simultaneously trying to get a family started and provide their livelihood does not do it without the real help that only a patient and durable wife can provide, and so it will be that in giving the proceeds of the award to my wife it will be because her efforts were a vital and major contribution.

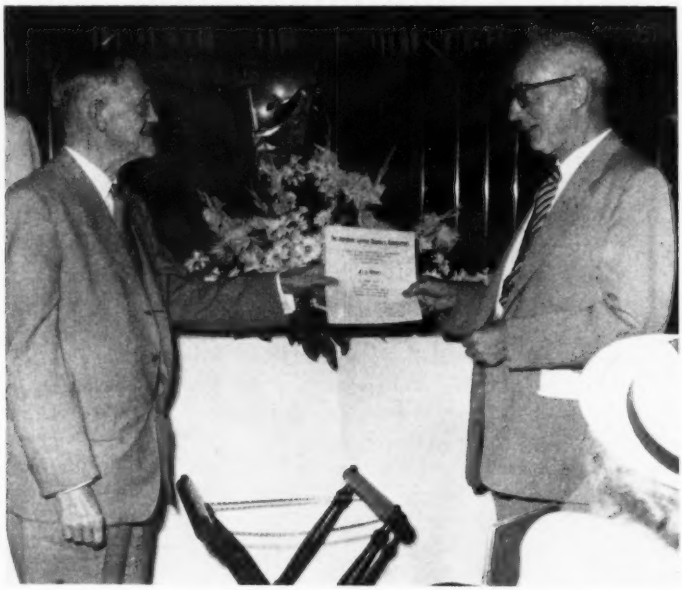
In addition, many of you will visit the Tanners' Council Research Laboratory tomorrow. After that visit you will understand why the physical and intellectual environment that is present there is conducive to bringing out one's best effort. The counsel, guidance, and genuine friendship that is

available to all graduate students and staff personnel at the Laboratory from Dr. O'Flaherty, Dr. Roddy, and Dr. Lollar, is probably something that is hard to equal anywhere.

It is for these reasons that the award is so deeply appreciated. Thank you once again."

DR. TURLEY

"It is now timely that we properly recognize the services of our members who have supported the Association for many years by their sustained membership. From them the Association, not only in the past but at present, continues to receive valuable advice on conducting the affairs of the Asssociation. To signalize their long and loyal service, Council has the power to bestow on them Life Memberships in the Association. To our present Life Members we are adding this evening, and so honoring the following members: L. C. Scott, John M. Seltzer, E. J. White, Boyd F. Gunnison, Adolf Schubert, Roy A. Wisdom, J. Edgar Rhoads. Unfortunately, due to unforeseen circumstances, we are presenting only two this evening, and the certificates will be mailed to the others. It seems most appropriate that one of our oldest members, Mr. Caspar Drueding, should present these certificates, and we are asking Mr. Drueding to kindly come forward and make the presentations."



Presentation of Life Membership Certificate to Mr. E. J. White by Mr. Casper Drueding.

Life Membership Certificates were presented to John M. Seltzer and E. J. White.

DR. TURLEY

"Ladies and Gentlemen it has been an unusual pleasure for me to be with you this evening and to receive these very fine tributes to our Association. It is particularly heart warming to have the presentation of the awards to such outstanding individuals.

Our part for the evening is over, but we call to your attention that tomorrow the Association is honoring the Thirtieth Anniversary of the foundation of the Tanners' Council Research Laboratory and we urge as many of you as possible to make this visit and so honor this outstanding institute of leather research.

Uni- and Multi-Point Binding of Chromium Complexes by Collagen and the Problem of Cross-Linking*

By K. H. GUSTAVSON

Garverinäringens Forskningsinstitut,
Stockholm, Sweden

1. INTRODUCTION

In studies of reactions of insoluble proteins, such as collagen with various solutes, as for instance, polyvalent electrolytes, the first problem is generally to locate the protein groups serving as sites for the binding of the agents on the protein. That problem is not too difficult as a rule and the specific groups of collagen involved in the fixation of a great number of tanning agents and other reactants are by now established with a fair degree of certainty. The second question of primary and current interest concerns the extent of binding of polyvalent electrolytes and tanning agents generally, both simple molecules such as formaldehyde and large complicated ones, such as the vegetable tannins, to collagen, *i. e.*, how many of the available valences of the agent partake in the binding and the number of cross-links formed.

How many of the multi-pointly attached molecules or complexes of a tanning agent actually effect cross-linking of the protein is a very difficult problem which only can be approached in a roundabout way, since for its solution, *inter alia*, knowledge of the distance between the protein groups involved and spatial details of the collagen structure are essential, which information is largely lacking. From the point of view of stabilization of the collagen lattice by crosslinking of polypeptide chains and other primary

*Presented at the Golden Jubilee Meeting of the A.L.C.A. in Cincinnati, Ohio, June 8, 1953.

units, the distance between the reacting groups of adjacent chains is the principal aspect, apart from the size of the agent interacting, the distance between its polyfunctional groups and its orientation in the lattice. The distance between any given group, for instance the carboxyl, on the same molecular chain may be inferred or approximated if certain assumptions are made. However, this particular case of reactions resulting in *intramolecular* linking of the tanning agent does not command so much attention as the *intermolecular* or *crosslinking* reactions of any agent, from the particular point of view of tanning potency. Since the conception of the configuration of the collagen chains is in a state of flux at the present time, particularly as a result of the introduction of the helical model by Pauling and Corey [1], further modified by Bear [2] and by Randall [3], any attempt of assessing the intermolecular distances of any particular group and the space factors generally should be premature. In spite of these difficulties, it is possible to get some insight into the reactions of tanning agents with collagen as regards the general classification of the reactions as (1) *Unifunctional, i. e.*, the molecule or ion is only attached to one reactive group of collagen. (2.) *Multifunctional, i. e.*, the attachment of the molecule or ion of the agent, fixed by collagen, to at least two reactive protein groups. The former type of interaction may in many instances, depending on the particular protein groups involved, result in labilization of the protein, a type of hydrotropy, whereas the multipoint binding of the agent by two or more protein chains will lead to stabilization of collagen, *i. e.*, tanning.

2. Experimental Evidence for Crosslinking of Globular Proteins

In order to secure a firm basis of reasoning, it seems advisable to state briefly the main experimental evidence in support of the concept of crosslinking reactions taking place in tanning of proteins. The increased stability of the proteins, as evidenced by the degree of hydrothermal stability and improved resistance to proteinases, cannot be considered to prove the thesis. The conclusive evidence comes from investigations of soluble proteins. The first demonstration was given by Fraenkel-Conrat and Mecham [4], who could prove intermolecular crosslinking of molecules of serum albumin and egg albumin in concentrated solutions (10 per cent) after interaction of formaldehyde, through the marked increase of the mean molecular weight of the treated proteins, evaluated by osmotic pressure measurement. Thus, for instance, by treating a ten per cent solution of serum albumin with 4.4 per cent formaldehyde, the mean molecular weight of the protein increased from 41,000 to 330,000, or eightfold. However, the solutions of one per cent strength of albumin after receiving the identical treatment with formaldehyde showed only a slightly increased molecular weight (to 61,000). That proves the importance of the close packing of the protein molecules in the solution

in order to provide better opportunity of bridging the colliding molecules by formaldehyde (cross-linking). The governing importance of the concentration of the protein solution and the spatial conditions are also shown in the interaction of chromium sulfate with gelatin solution, with resulting cross-linking (increased molecular weight) of the gelatin molecules by chromium complexes, as will be shown later.

The crosslinking function of vegetable tannins (tannic acid) on globulins, and albumin has been experimentally demonstrated by Danielsson [5]. The precipitates formed at pH 6 - 7, after being dissolved at pH 9, gave in the ultracentrifugal examination sedimentation constants more than 25 per cent higher than that of the pure albumin.

The third proof which pertains to the effect of chromium sulfates on gelatin solutions, has recently been given by Pouradier and his associates [6]. From osmotic pressure measurements on a 10 per cent solution of gelatin, with a mean molecular weight of 65,000, at 38 °C and pH 4.75, it was found that the addition of 1.5 per cent Cr_2O_3, on the weight of the gelatin increased the mean molecular weight of the chromed gelatin to 88,000 - 95,000. It is of interest to note that only about one per cent Cr_2O_3, which was the amount of chrome fixed by gelatin, suffices for such a marked crosslinking of the gelatin molecules. Pouradier also found that crosslinking does not occur in dilute solutions of gelatin of pH 5 (1 - 2 per cent solutions), an observation agreeing with the finding of Fraenkel-Conrat and Mecham regarding the formaldehyde-protein systems just mentioned. In these dilute gelatin solutions, any particular chromium complex is fixed and attached to *one* molecular chain of the protein, the *intramolecular* type of reaction. In concentrated solutions of gelatin, the close approach of the molecules and hence the steric conditions favor the intermolecular type of reaction of the chromium complex. This is proved by the increased molecular weight, as well as by the properties of the solution and the gel formed, particularly its viscosity, jelly strength and melting point.

Also the pH of the gelatin solution has a marked effect on the type of binding of complex chromium cations by the gelatin molecule, whether *inter-* or *intra-molecular*. In the isoelectric state, the gelatin chains are present in the contracted configuration, as a result of the attraction operating between oppositely charged groups of each molecular chain, and the internal hydrogen bonding. By the addition of acid, the formation of a net positive charge distributed along the chain will cause extension of the chain, since the excess charges repel. Experimental support of this view has been given very recently by Stainsby [7]. It is virtually an extension of the concept advanced by Werner Kuhn and A. Katchalsky [8] to explain the finding that by ionization of the carboxyl groups of polymetacrylic acid, by adding alkali to the solution, the neutral coiled molecule opens up, and extends under the influences of the repulsive forces operating between the charged groups formed.

In view of these facts regarding the shape of the gelatin chain at various pH values, the following findings of Pouradier are noteworthy. Gelatin in 0.85 per cent solution of pH 4.8 - 5.0 combines with chromium sulfate. However, *no* tanning effect is produced. In the corresponding solution adjusted to pH 4.0. a marked tanning effect is produced by the identical amount of chromium. The explanation is given by the schematic drawing of Fig. 1. In isoelectric state, the coiled gelatin chains favor sterically the binding of the chromium complex on *one* chain (intramolecular binding) whereas the form of the extended chain in the acidified solution allows two or several chains to react with one polyfunctional chromium complex under crosslinking (intermolecular binding).

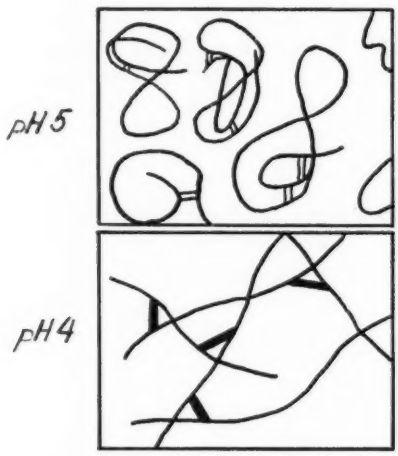
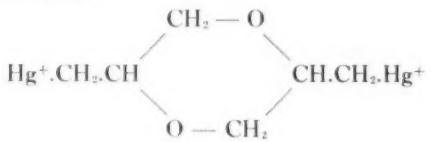


FIGURE 1.—The binding of chromium complexes by gelatin, in one per cent solution:
at pH 5: = **intramolecularly**
at pH 4: = **intermolecularly** (**crosslinking**) (**Pouradier**[6])

Another case of crosslinking watersoluble proteins by metals is exemplified by Hg^{2+} ions, which, for example, can crosslink two monomers of serum albumin into the dimer, with the formation of mercaptalbumins. This dimerization has been proved by a number of physicochemical determinations. An exceedingly powerful crosslinking agent is the dioxane derivative of mercury [9]:



The dimer-monomer systems of protein complexes with mercury and zinc (the imidazole group of the histidine residue being the site of attachment in the last instance) are completely reversible. Since the agents do not denature the protein, they have found use in preparative protein chemistry [9].

3. Experimental Indications of Crosslinking of Collagen by Tanning Agents.

In a solid protein, such as collagen, the steric influence of the protein chains on the crosslinking by chromium is more difficult to demonstrate unambiguously. However, by swelling of collagen to a limited extent, not jeopardizing the diffusion of the chromium salt through the pelt, the shrinkage temperature and stability in the boiling test (area shrinkage) are drastically impaired. It has been shown [10] that it is impossible to produce a leather standing the boiling test by means of the ordinary type of chrome tanning agents if the swelling of the pelt is maintained during the chrome tanning, although the amount of chromium fixed and the composition of the resulting leather are identical with those of the leather obtained by tanning pelt in the normal flaccid state under identical conditions.

The explanation given pointed to the possibility of unfavorable steric conditions being created by the contraction of the protein chains by swelling, preventing or impairing the crosslinking of adjacent chains, the distance between the reactive groups of adjacent chains being too great to be bridged.

These findings have been verified and extended by Holland [11], who found that extensive retannage of chrome leather, which had been tanned in swollen condition, by means of basic chromium sulfate, showing 54 per cent loss of area in the "boiling test", would not materially improve its stability to boiling water, giving 45 per cent shrinkage in the boiling test, at such large chromium contents as 23 per cent Cr_2O_3 on the weight of collagen. However, by the addition of adipate to the retanning bath, perfect stability of the leather to boiling water was procured. Evidently, the long chain of the adipate molecule, $-COO.(CH_2)_4.COO-$, enables crosslinks to be built up between two chromium complexes to overcome the steric hindrance of the distance between polypeptide chains in the swollen leather. Also the improved hydrothermal stability, obtained by treating leather of low hydrothermal stability, that of chromium chloride tannage for instance, in solutions of neutral sulfates [10] and salts of dicarboxylic acids such as adipate, succinate and fumarate [11], is likely due to the secondary formation of crosslinks by the chromium complexes, extended and enlarged by means of the bifunctional chains introduced.

These conclusions drawn from purely chemical evidence are given ample support by findings of the effect of tanning agents on collagen from the thermodynamic point of view; an important approach to the study of tanning reactions introduced by Weir [12] in his fundamental contributions, the value of which does not seem to be generally realized. By measuring the rate of

shrinkage of collagen and tanned collagen at four different temperatures, Weir found that chromium salts were unique in their behavior to collagen, since they greatly increased the heat of activation as well as the entropy and free energy of reaction. An important point to be discussed in connection with the present results was that the maximum effect, measured by the thermodynamic quantities, was obtained by incorporation of such a small amount of chromium as 1 per cent Cr_2O_3; larger amounts of fixed chromium giving lower energy values, *i. e.*, the stabilization of collagen was lowered. An excellent illustration of the different effects of unifunctional and bifunctional agents is given in the data of Weir and Carter [13] on the cyclohexane sulfonyl chlorides. The *mono*-sulfonyl chloride, combining with collagen without any chance of crosslinking, shows the same value of $\triangle H$, $\triangle S$ and $\triangle F$ as untreated collagen, whereas for the *bi*-functional sulfonyl chloride a decided increase in these thermodynamic quantities is noted.

Similar findings apply to the action of naphthalene sulfonic acids on the shrinkage temperature of collagen. Complete inactivation of the ionic groups of collagen by the non-swelling naphthalene-2-sulfonic acid, an *unifunctional* agent, decreases the shrinkage temperature of collagen 16 – 18°C, probably by complete rupture of the electrovalent crosslinks of collagen [14]. The disulfonic acids of polynaphthalenes, *bifunctional* agents, increase the Ts of collagen a few degrees, indicative of their function as crosslinking agents [15].

Another drastic example is afforded by the anionic, complex chromium compound, the hexathiocyanato chromiate, $Cr(CNS)_6^{-3}$ [16]. By its fixation in the collagen structure, the Ts is lowered a few degrees, if the Ts determination is carried out by the shocking method. By gradual heating of the chromiated stock, Ts increases up to 15°C are recorded. During the heating of the chromed pelt in the Ts-determination as carried out by the regular method, or by washing the "tanned" stock, polynuclear hydroxo-complexes are formed which are able to crosslink the collagen chains [16].

It appears a marked tanning effect connotes increase in some or all of the thermodynamic quantities, $\triangle F$, $\triangle S$, and even $\triangle H$. On the other hand, labilization of the collagen structure by lyotropic agents, or by swelling and disorganization generally, shows up in diminished values of these thermodynamic quantities [13]; the degree of organization of the protein chains evidently being a problem of entropy changes.

An important contribution based on entropy changes of polymers, applied to the shrinkage of collagen, is the recent paper by Wright and Wiederhorn [17]. Their data indicate that intact collagen contains about 600 amino acid residues between points of crosslinking. For collagen tanned by means of formaldehyde at pH 5 – 7, there are correspondingly some 200 residues between each crosslink, indicating the formation of additional crosslinks through the introduction of formaldehyde. The formation of one stable crosslink by formaldehyde on every 200 amino acid residue would probably necessitate the

interaction of the main part of the formaldehyde-binding groups in order to establish that crucial crosslink by the **normal** type of formaldehyde tannage.

A great many examples of protein reactions forming indications of crosslinking of other fibrous proteins are to be found in the textile field [18]. The introduction of crosslinking agents, some novel and chemically unique, into wool (keratin) has attained practical importance.

It must be admitted that the concept of crosslinking has been applied in many instances uncritically, without sufficient experimental support, even purely speculatively. Critical appraisal of this concept is therefore appropriate. The most important argument against the explanation of tanning processes and stabilization of collagen in terms of crosslinking has been advanced by Highberger [19], who found that by tanning of tendon by means of formaldehyde or quinone the tensile strength of the dry fibers was markedly decreased. These findings caused Highberger to question the general validity of, and the applicability of the crosslinking concept of the tanning mechanism to the mechanical stability of fibrous proteins, since the effect predicted on the basis of crosslinking appeared to be at variance with the findings. Later, the fundamental work from Highberger's laboratory [17] has necessitated revision of Highberger's original view [20]. Recent results of Roddy [21] indicate that the dry strength of collagen fibers is not altered by tanning. Since the *wet* strength is more significant, it is interesting to note, that Jacobson and Lollar [22] report that the wet strength of collagen fibers may be increased, or decreased by tanning. In many instances practically no effect of the tanning agents on the mean breaking length of wet collagen fibers was found. As pointed out in earlier papers [23], the hydrothermal stability of collagen is probably governed by the degree of crosslinking of the polypeptide chains and primary units (protofibrils) whereas the tensile strength of the fiber primarily appears to be a function of the cohesive forces between the larger units, fibrils and fibers. Thus, no direct relationship between hydrothermal stability and mechanical strength of collagen is to be expected. This dualism would imply that the fiber strength should be practically independent of the degree of crosslinking of the collagen molecule. The surface friction of the fibers is likely more important for the mechanical strength of the fibers, in view of the irregular effects of various tanning agents on the wet strength of collagen fibers [18].

4. The Extent of Crosslinking and the Proportion of Uni- and Multi-point Binding of Tanning Agents.

Considering the steric possibilities in the collagen lattice for establishing crosslinks between polypeptide chains and between protofibrils, the intrafibrillar penetration of the tanning agent is a primary requirement. In the case of formaldehyde and chromium salts of acidities >60 per cent, such penetration is indicated to occur regularly [2]. Providing such intrafibrillar

reactions take place, the approximate number of crosslinks formed out of the total number of fixed chromium complexes is of the utmost importance. From our present information regarding some fundamental issues of chrome tanning, such as the amount of chromium fixed by collagen from solutions of various chromium chlorides and sulfates, the mean charge of the complexes and the amount of carboxyl groups available for binding, an approximation of the types of binding and their relative proportion is feasible.

Before presenting the experimental data, an incident in the early development of the crosslinking concept back in 1940 will be briefly recalled, regarding that part of the total amount of tanning agent fixed by collagen, which is present in a state of combination effecting crosslinking. It was pointed out in a paper on the tanning power of aldehydes [24], that the fixation of the main part of the formaldehyde by the basic protein groups should not have any direct effect on the rigidity and stability of the protein. The tanning action, as measured by Ts, would then be restricted to those few uncharged basic groups which are sterically capable of crosslinking adjacent collagen chains. A comparatively large fixation of formaldehyde should than be required for the inactivation of all reactive basic groups, as to enable the very few groups of close proximity to react with formaldehyde by crosslinking. The well-known fact was stressed that the properties of linear polymers, such as polystyrenes, are drastically altered by the copolymerization of small amounts of a crosslinking agent, in this instance divinyl benzene, which added in an amount of 0.003 per cent on the weight of the polystyrene turns the benzene soluble product into a gel of highly developed structural restraint [25].

This reasoning has recently obtained experimental verification by the work of Wright and Wiederhorn [17]. In the collagen tanned by formaldehyde at pH 5 - 7, the figures show one crosslink to be present per 200 amino acid units. With a mean chemical molecular weight of collagen of 38,000 [26], the molecule should contain 12 lysine residues, the groups primarily involved under the given conditions of tanning. This molecule of collagen will contain in all about 420 amino acid residues. Hence the figures show that *two* crosslinks have been introduced into the collagen molecule by the bifunctional fixation of formaldehyde, which implies that only one sixth of the available number of ϵ - amino groups of lysine are crosslinking. Since the lysine equivalent is 0.31 meq. per g. collagen and that should be the maximum formaldehyde fixation by the lysine amino group, the amount of formaldehyde effective in crosslinking is calculated to be 0.05 meq. CH_2O per g. protein. The main part of the formaldehyde is probably uni-pointly fixed by collagen as methylol compound.

In his original studies of the interaction of salts of heavy metals with gelatin Elöd [27] found a very small percentage of chromium, 0.3 per cent Cr_2O_3 on the weight of gelatin, to be sufficient for making it resistant to boiling water. That is, provided the interaction takes place in systems devoid

of steric hindrance, such as in solutions of gelatin, which subsequently are made into films. Then, even such minute amounts as 0.03 per cent Cr_2O_3 had a marked effect. Since the minimum amount of chromium in fully tanned chrome leather is generally considered to be 3.4 per cent Cr_2O_3, on the basis of protein, it is indicated by Elöd's data that only about one tenth of this amount is the effective tanning agent; the incorporation of the large amount of fixed chromium being necessary for securing the effective type of binding, probably due to unfavorable steric conditions of the collagen lattice for such reactions. It is interesting to note that in dechroming chrome leather a small amount of the fixed chromium, or about 0.3 per cent, is very difficult to remove, showing markedly greater tenacity than the bulk of the chromium held by the leather.

5. Results and Discussion

Information on the general type of chrome fixation, prevailing in reactions of collagen with cationic chromium salts, particularly regarding the mean equivalent weight of the chromium complexes fixed by collagen may be obtained from the following considerations and data, on the assumption that the reactions are restricted to the carboxyl ions of collagen [3 5]. The average charge of the electropositive chromium complexes in solutions of basic chromium salts can be determined by the ion exchange technique [2 8], and hence the equivalent weight of chromium in these complexes. The average number of chromium atoms in the molecules of basic chromium salts may be obtained from determination of the coefficient of diffusion [2 9]. Since there are 2 – 4 atoms of chromium in the ordinary type of complexes, their dimensions will be of the order of 6 - 12 Å. The *maximum* amount of carboxyl ions of collagen available for binding the cationic chromium complexes is also known [2 6], although the proportion of charged carboxyl groups participating in the binding of chromium complexes and protons at a certain pH value in a given reaction cannot be ascertained by the methods presently available. Nevertheless, a probable mean value of the equivalent weight of the fixed chromium complexes can be approximated from data on the chrome fixation by collagen, assuming all carboxyl ions to be involved. The steric factors which are prominent in collagen, introduce elements of uncertainty and severe complications in such estimates. However, these may be largely eliminated by using dilute gelatin solution, in which all reactive groups should be completely accessible, for study of the chrome fixation, making use of cation exchangers as will be described in the following sections. The reactions of chromium complexes with gelatin in solution will hence give an idealized and simplified picture of the pure chemical aspect of the process of chrome tanning.

A. Chromium chlorides

A representative series of results from a solution of a 67 per cent acid chromium chloride will illustrate the principles of the method. The basic

chromium chloride was prepared by dissolving freshly precipitated hydrous chromium oxide in a boiling solution of the required amount of hydrochloric acid. The equilibrated solution contained 1.00 eq./1. Cr (25.3 g./1. Cr_2O_3).

Ion exchange. By the standard method of ion exchange in column, employing Dowex-50 in the sodium cycle [30], the solution was found to contain all its chromium in the form of cationic complexes. No complexly bound chloride was found. Thus, the mean composition of the cations corresponds to the empirical formula: $(Cr_2(OH)_2)^{4+}$. A direct determination of the equivalent weight was carried out by the following standard method. A portion of moist Dowex-50 (= 1 g. dry resin), employed as the ammonium salt (capacity: 5.0 meq. NH_4^+ per g. dry resin) was shaken for one hour with 4.0 ml. of the solution of the chromium chloride (= 4.00 meq. Cr or 101.2 mg. Cr_2O_3) diluted with 6.0 ml. water. The filtrate and washings were collected in a 200 ml. volumetric flask. In aliquots the contents of chromium and ammonium were determined. The amount of chromium fixed by the resin (indirectly determined) was 92.0 mg. Cr_2O_3. The amount of ammonium ions displaced by the chromium complexes from the resin, present in the solution, was 2.36 meq. Accordingly, the mean equivalent weight of the chromium complexes fixed in terms of Cr_2O_3 was 39, whereas the formula given requires 38.

Chroming of gelatin in solution. The following standard method was used: 10.0 ml. portions of 1.00 per cent gelatin (= 0.86 per cent protein) were treated for one hour with 1.0 ml. of the standard solution of the aforementioned chromium chloride (= 25.3 mg. Cr_2O_3). The chromed solution was freed from uncombined chromium by adding 3.0 g. moist Dowex-50 as the sodium salt (= 1.8 g. dry resin), shaking violently for 20 minutes and collecting the filtrate and washings in a 100 ml. volumetric flask. The filtrate contained all its chromium in combination with the gelatin. The amount of resin was well in excess of the amount required for complete removal of the entire chromium, which was ascertained through corresponding runs with water solutions of the chromium chloride. The gelatin solution contained 13 – 14 per cent Cr_2O_3 in combination with gelatin. Since gelatin contains 1.0 – 1.1 meq. carboxyl ions per g. gelatin, assuming 90 per cent of these groups to be present as COO^- at the pH value of 3.4 employed and to have reacted completely with chromium, values of the mean equivalent weight of 130 – 150, in terms of Cr_2O_3, are obtained for the cationic chromium complexes fixed by gelatin. Hence, the overwhelming part of the chromium complexes must be fixed by the gelatin in the form of complexes of the general type: $[Cr_2(OH)_2]Cl_3^+$.

With the mean equivalent weight of 38 for the cationic complexes present in the solution, expressed as Cr_2O_3 $\left(\frac{[Cr_2(OH)_2]^{4+}}{4}\right)$, the maximum amount of

chromium bound by gelatin should only be about 4 per cent Cr_2O_3, assuming the cation to react as a tetravalent complex with gelatin.

Accordingly, it is indicated, that in systems with readily accessible reactive protein groups, such as proteins in dilute solution, the basic chromium chloride behaves towards the protein as an unifunctional agent. Mainly on account of the variations of the equivalent weight of the fixed chromium and lack of data on the number of carboxyl ions of gelatin directly involved in the chrome fixation, no definite figure can be given, as to how large the percentage of chromium interacting bifunctionally with gelatin is, and still less what part of this fraction functions as a crosslinking agent. Nevertheless, the data indicate that only a few per cent of the total amount of chromium taken up by gelatin is fixed as a polyfunctional agent. That would mean that only some few tenth of one per cent of chromium oxide, based on the weight of the protein, is present in such a state in the chromed gelatin. This approximation appears reasonable in view of the findings of Elöd that the minimum amount of chromium necessary for making gelatin resistant to boiling water is of that order of magnitude, as already mentioned. The inability of basic chromium salts of acidities >50 per cent to precipitate gelatin solution is probably in some way connected with the predominance of the unifunctional binding of these chromium salts, besides the favorable conditions in the dilute gelatin solution for intramolecular reactions between the gelatin chain molecules and the chromium complexes.

Since the aforementioned type of unipointly bound complex should be expected to be less stable than a multipointly interacting complex it was deemed of interest to apply a cation exchanging resin with a stronger complexing group than the sulfonic acid group. The solution of gelatin containing chromium chloride as described was therefore reacted with 1 g. of a cation exchanger of the carboxylic type, Amberlite IRC-50. This was equilibrated with 2 M solution of sodium chloride of pH 6.5 and contained 4.8 meq. ionized carboxyl (as the sodium salt) and 5.6 meq. carboxyl groups in the unionized form [31]. The carboxyl ion of the resin is very aggressive towards chromium and should be expected to displace cationic complexes of low degree of attachment to the gelatin. The amount of chromium not removed by this resin amounted to 8.0 per cent Cr_2O_3 on the weight of the gelatin. The displacement of about half of the chromium found to be bound by gelatin by applying the sulfonic type of cation exchanger of relatively low complexing power, by the strong complexing carboxylic ion of the resin apparently indicates the presence of either carboxylic ions of different strength in collagen, or chromium complexes of various degrees of bonding strength in the chrome-protein compounds formed, or both possibilities. It is also possible by greatly increasing the ratio of the amount of sulfonic acid resin to the amount of chromium in the gelatin solution to displace smaller amounts of chromium from the chromed gelatin.

An interesting example from the metal-amino acid interactions is the binding of Cu^{2+} and Zn^{2+} by the imidazole group of histidine. The first Cu^{2+} ion is bound much more strongly than the first Zn^{2+}. However, the binding of one imidazole by Cu^{2+} decreases the probability of binding the next, whereas the binding of the first imidazole by zinc increases its affinity for more imidazoles, until saturation is reached[32] with four molecules of histidine bound.

Chrome fixation by collagen. By tanning portions of hide powder (2.0 g.) in 50 ml. portions of solutions of the 67 per cent acid chromium chloride, 25.3 g./1. Cr_2O_3, for 24 hours (with final pH: 3.2), the amount of chromium fixed was 9.6 per cent, on the weight of collagen. The content of chloride was 7.4 per cent Cl, on the same basis. Since the binding capacity of collagen for hydrochloric acid is 0.9 meq. HCl per g. collagen, (=3.2 per cent Cl), at least an amount of chloride groups equal to 4.2 per cent Cl, on the weight of collagen, must be associated with the chromium complexes fixed by collagen. Since according to the ion exchange analysis, the chloride quantitatively is in the ionic form, no chloro groups being present, also proved by the complete removal of chloride groups of the chromed hide powder by means of pyridine in 4 per cent aqueous solution (1 hour), the chloride groups in excess of the amount of the maximum combining capacity of collagen must be associated with the hydroxo-chromium complexes fixed by collagen as compensating ions to the positively charged chromium complexes attached to collagen through *one* carboxyl group.

The mean equivalent weight of the hydroxo-chromium complexes fixed by collagen should be of the order of 120 assuming 80 per cent of the available carboxyl groups (about 0.8 meq. per g. collagen) to be partaking in the binding at pH about 3. Unfortunately, no method is available for differentiating between free (proton-binding) and compensated carboxyl (chromium binding) groups in chrome leather. However, the data from the system: collagen—chromium chloride indicate the main part of the complexes reacting with collagen to be of the type: $(Cr_2(OH)_2)Cl_3^+$, and the minor part to be the corresponding forms with fewer compensating Cl-ions and the hydroxo-chromium cation. Further, the data are in accord with the view that only a small percentage of the chromium complexes reacting with collagen are interacting multifunctionally with crosslinking of the structure.

The relatively low degree of hydrothermal stability imparted to collagen in tanning with basic chromium chlorides, compared to the corresponding tanning with basic sulfates, may possibly be due to this preference of the cationic complexes of chromium chlorides for unipoint combination with collagen, in part at least.

The drastic improvement of the hydrothermal stability of chromium chloride-tanned leather by its subsequent treatment in solutions of salts of bifunctional carboxylic acids, such as adipate, was explained by Holland[11]

to be due to an increase in the number of cross linkages between the peptide chains, the bifunctional residue of the dicarboxylic acids joining two chromium complexes attached to two different polypeptide chains. This suggestion is supported by the present finding of the predominance of unipointly attached chromium complexes in collagen tanned with chromium chlorides. Thus, a chloride leather showing an area loss in the boiling test of 60 per cent, is made "boil-proof" after 2 days' immersion in a 0.25 M solution of sodium adipate. Since the length of an adipate bridge of the type: –Cr–O–Cr–OCO$(CH_2)_4$.OCO–.Cr–O–Cr– should be about 23Å, and the side-chain distance between protein chains of hydrated collagen is of the order of 17 Å, the steric conditions for the crosslinking are favorable. As a lucid illustration of the governing role of the spatial factor in crosslinking, the effect of salts of the geometrical isomers, maleic and fumaric acids, on the shrinkage temperature of leather tanned with chromium chloride, demonstrated by Holland [11], must be mentioned. The sodium salt of fumaric acid, with the carboxyl ions in the *trans* form: $\begin{matrix} COO^-.CH \\ \| \\ CH.COO^- \end{matrix}$ increases the Ts more than 20°C, whereas the maleate, with the carboxyls in the *cis* form, $\begin{matrix} CH.COO^- \\ \| \\ CH.COO^- \end{matrix}$ has hardly any effect on the Ts, apart from that due to its neutralizing action, in 2 days' treatment of chloride-leather in 0.25 M solutions of these salts. Hence, the *trans* position of the carboxyls in the fumarate provides spatial facilities for crosslinking.

It is interesting to note that the reaction between solutions of basic chromium chlorides and gelatin attains equilibrium very rapidly, in less than one minute's time, and that it is time-independent, while the corresponding system with basic chromium sulfates is highly time-dependent, requiring some few hours for attaining equilibrium, as evident from Fig. 2.

B. Chromium sulfates

The basic chromium sulfates investigated were:

(1) a neutral salt-free solution of the 67 per cent acid chromium sulfate. Its composition corresponded to the empirical formula: $Cr_2(OH)_2(SO_4)_2$. It was obtained by reducing equal moles of chromic acid, CrO_3, and sulfuric acid, H_2SO_4, with hydrogen peroxide (30 per cent) at 4 – 5 °C [33]. The equilibrated solution was adjusted to contain 1.00 eq. 1. Cr (25.3 g. 1. Cr_2O_3). It consisted of 98 per cent of cationic chromium complexes, the rest being non-ionic. The cationic sulfato-chromium complexes had an average acidity of 16 per cent, determined by means of cation exchange (Na-salt of Dowex-50) [30]. Determinations of the acidity of the sulfato-chromium cations by removal of the ionic sulfate by means of the quaternary anion exchanger

Amberlite IRA-400 (as HCl-compound), according to the standard method [34], gave average values of 32 per cent. Hence, about half of the sulfate groups are easily displaced by the sulfonic acid ions of the cation exchanger. Hence, the cationic complexes would correspond to the empirical formula: $(Cr_2(OH)_2SO_4)^{2+}$.

(2) Another type of the 67 per cent acid sulfate was prepared by reducing sodium bichromate with sulfur dioxide, in a concentration of 150 g./1. Cr_2O_3. After boiling and ageing of the stock solution, it was diluted to contain 25.3 g./1. Cr_2O_3 and aged for 4 weeks for equilibration. The equilibrated solution contained 90 per cent cationic complexes and 10 per cent non-ionic ones. The average sulfato-acidity of the cationic complexes was 33 per cent corresponding to complexes of the type $(Cr_2(OH)_2SO_4)^{2+}$, determined by the cation exchange technique. By removal of the anions by Amberlite IRA-400 as described [34], the mean acidity of the sulfato-chromium complexes was found to be 34 per cent. From analysis of the hide powder tanned by means of this solution and subsequently treated for removal of ionic sulfate with pyridine [35], an average acidity of the fixed sulfato-chromium complexes of 32 per cent was found whereas the neutalization-diffusion method gave 44 per cent, which finding will be discussed later on. By treatment of the chromed hide powder (2 g.) in 100 ml. 5 per cent aqueous aniline for 12 hours at final pH 5.5, the acidity of the treated specimen was reduced to 45 per cent.

Evidently, as pointed out in earlier papers [35], the neutral sulfate in the regular type of chrome liquors functions as a stabilizer of the sulfate groups in the chromium complexes. It has also been pointed out earlier that the sulfato-chromium complexes of acidity 33 per cent, contain half of its sulfate groups in a more stable combination than the other half [36].

Ion exchange. A direct determination of the mean charge of the cationic chromium complexes of the solution of the salt-free basic chromium sulfate (No. 1) was carried out by cation exchange, using the ammonium salt of Dowex-50. This method, based on estimating the equivalents NH_4-ions given off to the solution in exchange for the cationic chromium complexes taken up by the resin, can obviously not be applied to solutions of type No. 2, containing sodium ions also, since this introduces complications. In the present instance, 2.0 ml. of the stock solution (=50.6 mg. Cr_2O_3), diluted with 8.0 ml. water was shaken with an amount of moist resin equal to 1 g. dry substance for 10 minutes. A quantity of 35.2 mg. Cr_2O_3 was taken up and 0.69 meq. NH_4^+ given off. Hence, the equivalent weight of the chromium complexes reacting with the resin was 35.2:0.69=51, in terms of Cr_2O_3, which corresponds to a complex of the general type $\left(Cr_2(OH)_2\frac{SO_4}{2}\right)^{3+}$, of an equivalent weight of 50.7, as Cr_2O_3. Since by the anion exchange the

acidity of the sulfato-chromium cation was found to be about 33 per cent, and the fixation of a complex of this type by collagen also has been proved, the figure of complexes of mean acidity of the sulfato complex of 17 per cent, found in the above exchange experiments, is another example of the displacement of about half of the sulfato-groups of the cationic chromium complexes by the penetrating sulfonic acid group of the cation exchanger.

Chroming of gelatin. It was mentioned in discussing the behavior of chromium chlorides to gelatin solution, that the fixation of chromium by gelatin was time-independent; equilibrium being attained in one minute's interaction, as curve III in Fig. 2 shows. However, the time factor is clearly shown in the corresponding reactions of basic chromium sulfates, as curves I and II of Fig. 2 demonstrate. These data were obtained from series, in which 1.0 ml. of solutions of No. 1 and No. 2 (=25.3 mg. Cr_2O_3) were shaken with 10.0 ml. 1.0 per cent gelatin solution for various periods of time, the uncombined chromium being removed by means of 3.0 g. moist sodium-Dowex-50 (=1.8 g. dry substance), shaking for 20 minutes. Corrections were applied for the amounts of non-cationic chromium present in the solutions of basic chromium sulfate.

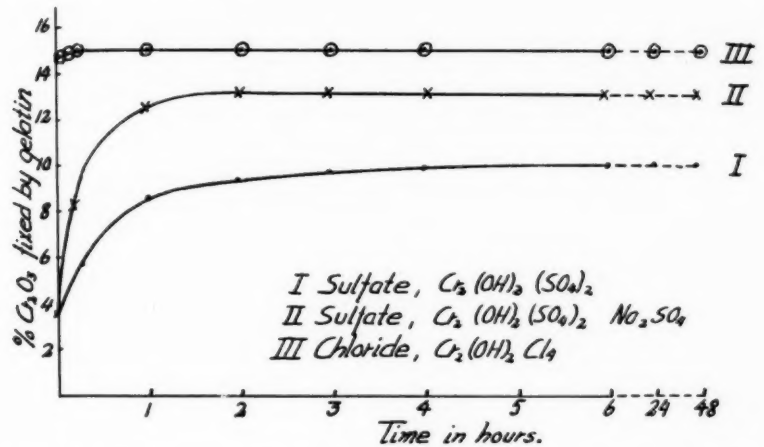


FIGURE 2.—The interaction of chromium salts with gelatin in one per cent solution as a function of time.
(Details in the text)

The curves for the sulfate solutions show that at least four hours are required for attainment of equilibrium. The cationic complexes of solution No. 2, represented by $(Cr_2(OH)_2SO_4)^{2+}$ should give a theoretical *maximum* binding of about 8 per cent Cr_2O_3 on the basis of gelatin, if these complexes

react as bivalent cations with gelatin. The figure of 13.2 per cent Cr_2O_3 combined with gelatin evidently proves beyond any doubt that the largest part of the fixation takes place as unipoint binding of cations of the type $[Cr_2(OH)_2SO_4]\frac{SO_4^{+}}{2}$. Still, the multipoint interaction and binding, necessary for the crosslinking function of the chromium complexes is considerably more pronounced for basic sulfates than for the corresponding chlorides.

Chrome fixation by collagen. In tanning experiments carried out with the basic chromium sulfate (solution No. 2), limiting the duration of tanning to 24 hours in order to avoid secondary fixation in this case, collagen (hide powder) fixed 11.0 per cent Cr_2O_3 on protein basis. The total sulfate content was 13.7 per cent. By shaking the chromed hide powder (=2.0 g. collagen) in 50 ml. of 4 per cent solution of pyridine for one hour, the sulfate content was reduced to 6.7 per cent SO_4. Hence, an amount of 7.0 per cent SO_4 was present outside the chromium complexes, probably in the form of protein-bound sulfate and as sulfate ions compensating the charged chromium complexes attached to collagen. Since the maximum binding capacity of collagen for sulfuric acid at equilibrium pH > 1.2 is of the order of 5 per cent SO_4, on the basis of collagen, an amount of 2.0 per cent SO_4 should at least be present in the third form, assumed to function as "Gegenion" (compensating ion) of the charged, unipointly fixed sulfato-chromium complex. By applying the diffusion-neutralization method for removal of protein-bound acid by shaking the tanned hide powder (=2 g. collagen) in 250 ml. water for 48 hours, adding 0.1 N NaOH solution frequently in order to keep the pH value about 5 (methyl red), the neutralized stock contained 9.2 per cent SO_4, on the weight of the protein. Providing the protein bound acid is mainly removed in this treatment, the protein-bound acid is figured to be about 4.5 per cent SO_4 on protein basis. The 5 per cent aqueous aniline showed the same order of effectiveness in removal of ionic sulfate upon 12 hours' shaking of the stock.

In running the diffusion-neutralization method at pH 8.2 (phenolphthalein as indicator) for 24 hours, the neutralized hide powder retained 6.2 per cent SO_4, which corresponds to an average acidity of the sulfato-chromium complexes of 30 per cent, a value in good agreement with that of the pyridine extracted specimen.

The mode of attachment of the sulfate groups which are removed in the reactions between pH 5 and 8 is not known. However, the possibilities are probably the two mentioned above. The proportion of these two kinds of sulfate groups is an important issue. Since the isoelectric point of collagen chromed by means of cationic chromium sulfate is in the pH range 7 – 8, treatment for complete removal of ionic sulfate should be carried out in this pH range. If that is done, however, the amount of protein bound acid will greatly

exceed the maximum binding capacity of collagen for sulfuric acid (in systems of pH > 1.2). However, a basis for the arithmetic of the system is obtained by alloting a value of 5 per cent SO_4 on the basis of collagen, *i. e.*, the maximum binding capacity of this protein for sulfuric acid at pH > 1.2, for the protein-bound sulfate.

The figures and theorizing are based on the assumption that the fixation of cationic chromium complexes by collagen occurs through the carboxyl ions of the protein entirely [38]. Basing the calculations on the figures given above and assuming 80 per cent of the carboxyl ions of collagen at a final pH of about 3.2, (0.8 meq. per g. collagen) to partake in the fixation of the cationic chromium complexes, the complexes fixed by collagen are found to consist of about 20 per cent of bi-pointly fixed $(Cr_2(OH)_2SO_4)^-$ complexes (=1.2 per cent Cr_2O_3, on the basis of protein), and of 80 per cent of unipointly attached complexes of the general type: $(Cr_2(OH)_2SO_4)\ \frac{SO_4}{2}$ (9.8 per cent Cr_2O_3). These figures are based on the amount of available carboxyl groups. Hence, the amount of Cr_2O_3 incorporated with collagen is composed of about 90 per cent of the unifunctional complexes carrying residual electrical charge and of 10 per cent of bifunctional complexes, both of their valences being compensated by the carboxyl of collagen.

The crosslinking complexes are to be found in the one per cent chromium oxide which is bipointly fixed by collagen. Although the uncertain factor in these calculations is the amount of carboxyl ions of collagen reacting with chromium, the approximation given above, assuming about 80 per cent of the carboxyl groups to react with chromium at a pH of ca. 3.2, is probably not very far off. It is hoped that work now in progress aiming at procedures for determination of the amounts of free carboxyl groups in chrome leather and for distinguishing between anions of the acid bound to the protein and to the chromium complexes by ionic forces, will eliminate this factor of uncertainty in the synopsis of data and hence make it possible to estimate accurately the proportion of the uni- and multipoint attached chromium complexes in chrome leather. The next problem will then be to ascertain how many of the multipointly fixed chromium complexes stabilize the collagen lattice by crosslinking adjacent protein chains.

It is well-known that by proper tanning, leather containing 3 – 4 per cent Cr_2O_3 on the weight of hide substance withstands the action of water of 95 – 100°C, even the boiling test. Additional fixation of chromium does not add materially to the hydrothermal stability. Further, such a small amount of Cr_2O_3 as one per cent, on the weight of collagen, radically improves the stability of collagen. Apparently, the initially fixed chromium complexes are preferentially reacting with those carboxyl groups which are favorably located on adjacent protein chains for interaction with the same chromium complex, which is estimated to have a length of 6 - 12 Å. These bipointly

attached complexes are the effective tanning agent. It is interesting to note that information on the vegetable tannage (mimosa) also points to the initially fixed tannins as mainly effecting the stabilization of collagen in that tannage. Although the great majority of the vegetable tannins probably are attached to the peptide bonds, the small fraction of great avidity for collagen first fixed, which appears to be responsible for the crosslinking, is indicated to combine with the basic protein groups mainly [37]. Weir's rather puzzling findings, mentioned earlier, that the optimal hydrothermal stability of collagen is attained by its fixation of such small amounts of chromium as one per cent Cr_2O_3, evaluated by data on the thermodynamic quantities, also appears in a new light. The crosslinking is mainly effected by the small amount of chromium incorporated in the collagen lattice. The decreased stability of collagen indicated by Weir's data to result from binding of large amounts of chromium will then be explained by the predominance of unipoint binding of chromium complexes by single carboxyl groups which connotes rupture and elimination of a part of the ionic crosslinks of the original collagen, which bridges in a small way contribute to the organization of the protein structure.

In his lucid contribution [12], Weir stated that only a fraction of the acidic and basic protein groups possess the required spatial orientation to react with the chromium complexes to form crosslinks. He suggested that the amount of chromium combined with collagen in excess of one per cent probably combines with collagen in the same manner as the other types of tanning agents do, decreasing the entropy of activation. Finally, Weir concluded, that this additional chrome will add nothing to the orientation of the protein chains and their stabilization. On the contrary, incorporation of large amounts of chromium will mean some loss of orientation of the protein lattice. These suggestions are in harmony with the findings reported in this paper and with the concept of the dual nature of the chrome fixation based on the present experimental data.

Summary

The experimental evidence for crosslinking of proteins, particularly gelatin and collagen, is reviewed.

It is indicated from the study of the interaction of cationic basic chromium salts with gelatin in dilute solution that the chromium complexes combining with gelatin (the uncombined chromium being removed by ion exchanging resins) from solutions of basic chromium chlorides containing entirely complexes of the type: $(Cr_2(OH)_2)^{4+}$, preponderantly are reacting unifunctionally; the cation $(Cr_2(OH)_2)Cl_3^+$, being mainly fixed by gelatin. The corresponding basic sulfate is fixed by gelatin to the largest part (about 80 per cent)

as unifunctional cations of the general type: $(Cr_2(OH)_2SO_4)\frac{SO_4^+}{2}$. The rest of chromium is indicated to be attached as $(Cr_2(OH)_2SO_4)$ complexes by two carboxyl groups of the protein.

From analysis of collagen (hide powder) tanned with basic chromium sulfates and determination of the mean charge of the chromium complexes and the acidity of their sulfato-chromium cations, an approximation of the proportion of uni- and bipointly bound chromium complexes in chrome leather is possible. In the special case of normal tannage exemplified, it is found that in hide powders, tanned with the basic sulfate to contain 11.0 per cent Cr_2O_3, on the basis of collagen, about 90 per cent of the total amount of chromium incorporated with collagen has been introduced in the form of unifunctional complexes. The rest of the combined chromium, or ca. one per cent Cr_2O_3 has combined with collagen in the form of bifunctional complexes.

The crosslinking chromium complexes must belong to the last mentioned fraction of fixed chromium. Since probably only part of these complexes are attached to carboxyls of different protein chains, for steric reasons, it appears as only a very small fraction of the chromium fixed by collagen is effecting the stabilization of the structure by means of its intermolecular attachment in the protein lattice and its crosslinking function.

Since such small amounts of combined chromium as one per cent Cr_2O_3 drastically improve the stability of collagen, apparently the initial chrome fixation is preferentially involving those carboxyl ions of adjacent chains, which sterically are able to combine with one chromium complex (crosslinking). This view is in harmony with Weir's finding by thermodynamic approach that the optimum stability of collagen is attained by its fixation of ca. one per cent chromic oxide; large amounts of bond chromium showing lower values of the thermodynamic quantities and hence, also lower degree of stability. This trend is conceivably due to the rupture and elimination of ionic crosslinks by the unipoint attachment of the main part of the chromium complexes to carboxyl ions of such salt-links, in the later stages of the tanning.

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References

1. Pauling, L., and Corey, R. B., *Proc. Natl. Acad. Sci. U. S.* **37,** 272 (1951).
2. Bear, R. S., *Adv. Protein Chem.* **7,** 69 (1952).
3. Randall, J. T., *et al*, *Nature* **169,** 1029 (1952).
4. Fraenkel-Conrat, H., and Mecham, D. K., *J. Biol. Chem.* **177,** 477 (1949).
5. Danielsson, C. E., *Svensk Kem. Tidskr.* **60,** 142 (1948).
6. Pouradier, J., *et al*, *Bull. Soc. Chim.* 1952, p. 928 (preprint)
7. Stainsby, G., *Nature* **169,** 662 (1952).
8. Kuhn, W., *Experientia* **5,** 318 (1949);
   Kuhn, W., *et al*, *J. Polymer Sci.* **5,** 283 (1950);
   Katchalsky, A., *Ibid.* **7,** 393 (1951).
9. Straessle, R., *J. Am. Chem. Soc.* **73,** 504 (1951); See also:
   Hughes Jr., W. L., *Ibid.* **69,** 1836 (1947) and
   Edsall, J. T., ref. (32).
10. Gustavson, K. H., "Stiasny Festschrift", 1937, pp. 117-131.
11. Holland, H. C., *J.I.S.L.T.C.* **24,** 22 (1940).
12. Weir, C. E., *J. Research N.B.S.* **42,** 17 (1949); *J.A.L.C.A.* **44,** 142 (1949).
13. Weir, C. E., and Carter, J., *J. Research N.B.S.* **44,** 599 (1950).
14. Gustavson, K. H., *Biochem. Z.* **311,** 347 (1942); *J.A.L.C.A.* **41,** 47 (1946).
15. Gustavson, K. H., *Ing. Vetenskaps Akad. Handling.* No. 177 (1944); *Svensk Kem. Tidskr.* **55,** 249 (1943); *J.A.L.C.A.* **41,** 47 (1946).
16. Gustavson, K. H., *Svensk Kem. Tidskr.* **62,** 1645 (1950).
17. Wright, B. A., and Wiederhorn, N. M., *J. Polymer Sci.* **7,** 105 (1951).
18. See, *e. g.*, Speakman, J. B., *J.S.L.T.C.* **37,** 37 (1953).
19. Highberger, J. H., *J.A.L.C.A.* **42,** 493 (1947).
20. Highberger, J. H., *J.A.L.C.A.* **47,** 108 (1952).
21. Roddy, W. T., *J.A.L.C.A.* **47,** 98 (1952).
22. Jacobson, K. H., and Lollar, R. M., *J.A.L.C.A.* **46,** 7 (1951).
23. Gustavson, K. H., *J.A.L.C.A.* **45,** 789 (1950).
24. Gustavson, K. H., *J.I.S.L.T.C.* **24,** 377 (1940).
25. Staudinger, H., "Zur Entwicklung der Chemie de Hochpolymeren", Berlin, 1937, p. 152.
26. Bowes, J. H., and Kenten, R. H., *Biochem. J.*, **43,** 363 (1948).
27. Elöd, E., and Schachowskoy, T., *Collegium*, **1933**, 701.
28. Gustavson, K. H., *Svensk Kem. Tidskr.* **56,** 14 (1944); *J.S.L.T.C.* **30,** 264 (1946); *J. Colloid Science* **1,** 397 (1946).
29. Riess, C., and Barth, K., *Collegium* **1935**, 62.
30. Gustavson, K. H., *J.S.L.T.C.* **35,** 160 (1951); *J.A.L.C.A.* **47,** 152 (1952).
31. Gustavson, K. H., *J.S.L.T.C.* **36,** 182 (1952).
32. Gurd, F., and Goodman, D. S., *J. Amer. Chem. Soc.* **74,** 670 (1952);
   Edsall, J. T., Discussions of the Faraday Society, No. 13, 1953. "The Physical Chemistry of Proteins", pp. 20-21.
33. Gustavson, K. H., *Svensk. Kem. Tidskr.* **58,** 2 (1946).
34. Gustavson, K. H., *J.S.L.T.S.* **35,** 270 (1951).
35. Gustavson, K. H., *Das Leder* **3,** 293 (1952).
36. Gustavson, K. H., *Svensk Kem. Tidskr.* **63,** 167 (1951).
37. Gustavson, K. H., and Nestvold, M., *Das Leder* **2,** 121 (1951); *J. Leather Tech. Assoc. India* **1,** 6 (1952); *J.S.L.T.C.* **36,** 105 (1952).
38. Gustavson, K. H., *J. Amer. Chem. Soc.* **74,** 4608 (1952).

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The Physical Characteristics of Chrome Tanned, Fatliquored Goatskin Leather

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INTRODUCTION

All tanners realize the importance of fatliquoring in providing some of the physical properties desired in leather. This process in leather manufacture has received only limited attention from a technological approach.

Those familiar with the literature have read the review on fatliquoring up through the year 1942 as given in the book by McLaughlin and Theis [1]. The chapter on fatliquoring considers the character and composition of oils and fats used as well as the extent of uptake and distribution of the fatliquor in leather. Since then additional research on lubrication of leather has been conducted and that pertaining to the fatliquoring of leather is listed below.

Koppenhoefer [2] reported on the role of various sulfated fatty oils in the fatliquoring of light chrome calf leather. The fatliquored leather was evaluated on the basis of oil take-up, oil distribution, tear resistance and resistance to aging. Marine and animal oils proved to be superior to vegetable oils as to the physical character of the leather and its tear resistance.

The application of German exchange fats as stuffing agents for Army side upper leather was reported to the tanners [3]. The exchange fats were screened and the better fatliquoring materials were used alone or admixed with natural fatliquoring materials on calfskins and provided leathers which were equivalent to the regular production leathers and held up at least as well during two years of storage.

Cox and Roddy [4] studied the effect of fat content on the dry adhesion of calfskin leather in a fundamental study of leather pasting. It was observed that the adhesion of the leather decreased with increased fat content in the grain area up to a level of 20 to 25 per cent on the hide substance basis.

Tannery pilot scale experiments by Roll [5] were reported on fatliquor distribution in chrome-vegetable retanned leather. He used both anionic and cationic type emulsifying agents and also considered the distribution of the fatliquoring during drying. It was found that the cationic fatliquoring on chrome-vegetable retanned leather resembled the behavior of sulfated oils on straight chrome tannages. Migration of oil during the drying of fatliquored leather did not alter appreciably the comparative oil distribution obtained in the wet leather.

Another set of experiments conducted on a tannery scale was reported by Pankhurst and coworkers [6] who considered the influence of fatliquor on spue

and run in gloving leather. (Reduction in width resulting from longitudinal stretching). Tentative conclusions were that more work is necessary before they can specify requirements of a spue-free fatliquor which gives good run in terms of physical and chemical constants.

Shuttleworth [7] considered the effect of lubrication on stitch tear strength of chrome retan leather. No significant differences were found in the ratio between tear strength increase and oil uptake.

Koppenhoefer [8] presented to the tanning industry information on the lubricating properties of mineral oils when used as replacements for fatty oils in fatliquoring. He concluded that from a strictly lubricating standpoint, mineral oil appears to be as effective as a typical fatty oil such as cod oil. It differs, decidedly, in its manner of distribution which fact is reflected in the pysical properties of the processed leather. Its value and effect depend on the quantity used and the type of leather being processed.

Most of the above experimental work conducted on fatliquoring has not taken into consideration the application of statistics. During the past year, however the work of Pankhurst and his associates [6] and of Shuttleworth [7] have been so designed and this has permitted more valid interpretation of the data.

It is the intention of this laboratory to do a comprehensive study of all phases of fatliquoring in a fundamental manner and to consider all types of stock concerned. For the purpose of developing statistically planned experiments permitting for sounder and broader conclusions, we have undertaken this one phase with goatskin leather.

Prior to starting a study of the fatliquoring process as it influenced the physical characteristics of goatskin leather it was felt that some basic data should be obtained on goatskin leather. A review of the literature revealed no specific information on the physical characteristics of fatliquored chrome tanned goatskin leather.

As there is variation in physical strength characteristics of calfskin leathers from area to area Koppenhoefer and Retzsch [9] used adjacent samples to minimize this variable in studying the behavior of the various components of fatliquors on the physical strength characteristics of calfskin leather. For the purpose of developing the best sampling plan we made the following approach.

It was felt that at least ten goatskins would be necessary to determine the between and within skin variation. Ten Amritsar goatskins of medium weight and ranging from 5-7 square feet per skin were obtained for this purpose from a tannery. Six additional Amritsar goatskins were obtained for a study of the relation between grease content of the leathers and their physical properties. The goatskins were selected from shoe lining stock which had been colored, fatliquored and dried.

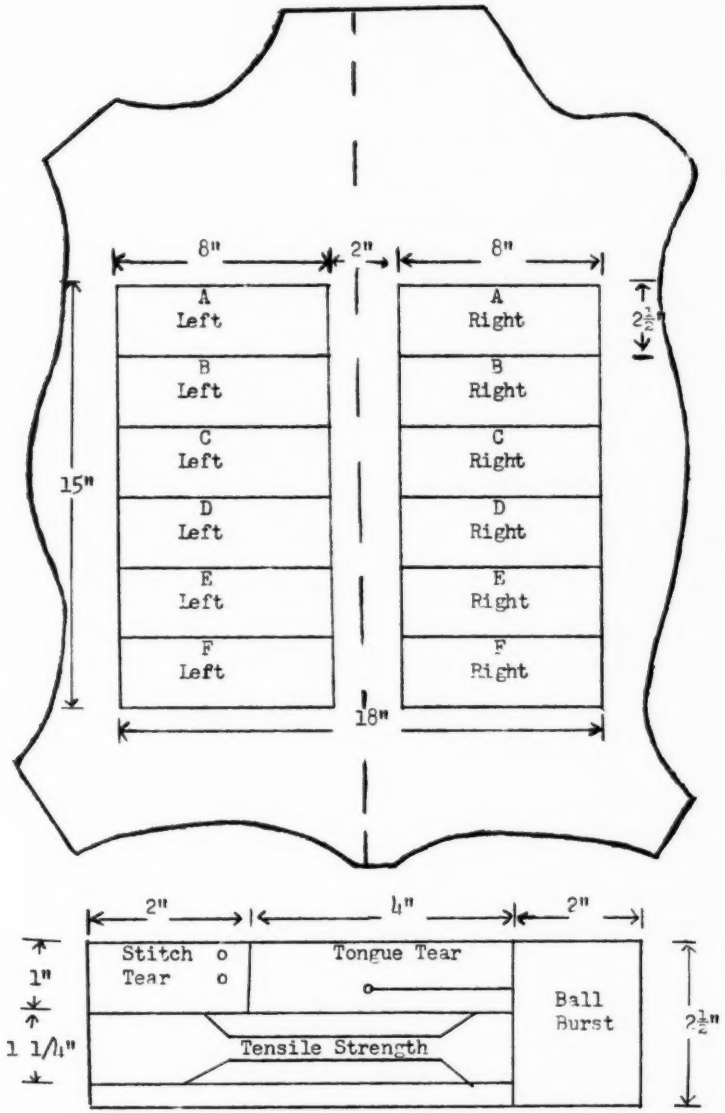

FIGURE 1.—Diagramatic Drawing of Samples Removed from the Respective Positions on the Skin and the Location of Physical Test Specimens Cut from Each Sample.

Experimental

From each of the first ten goatskin leathers received 12 samples of an area of 2.5 by 8 inches were cut as is shown in Figure 1. The location of the specimens from each sample for tensile strength, stitch tear strength, tongue tear strength [10], and ball burst strength are given in the lower part of Figure 1. The specimens were conditioned for 48 hours at 70°± 5°F. and at a relative humidity of 65 ± 2 per cent. After conditioning tensile strength, stitch tear strength and tongue tear strength were determined on the Scott tensile tester. The ball burst strength was determined on an apparatus developed by Vickers [11].

To obtain an indication of the relation of the fat content to the physical properties of the leather six more Amritsar goatskins were used. In this case a similar sampling procedure to the one shown in Figure I was used. The ball burst strength was determined on the end of the tensile strength specimen in order to confine the limits of the test area instead of using the larger specimen from the lower edge of the skin as used in the previous testing. The samples were conditioned and physical tests conducted as explained above. The compiled physical test data from the sixteen leathers were analyzed using a statistical three factor analysis of variance which took into account symmetry, skin and position [12].

The deposition of the fat through various layers of the skin was also determined. After physical testing the scrap and the broken ends of the physical test specimens from each position on the skins were split into three separate layers of approximately equal thickness which were designated as grain, corium and flesh layers. The three layers from each area were separately ground in a Micro-Wiley mill and then conditioned at 70° ± 5°F. and at a relative humidity of 65 ± 2 per cent for at least 48 hours.

Single moisture determinations were run in a Freas forced air oven at 100°C. for 16 hours. Grease determinations were run on other portions of the leather samples using a 16 hour extraction with chloroform in micro-soxhlets. Chloroform was used because it was found to extract more fat at a more rapid rate than petroleum or ethyl ether.

Results

The original data on strength characteristics for the sixteen skins are given in Tables I, II, III, and IV. The data are presented to show the variability of each skin from area to area for the respective physical properties, the symmetry which exists for each skin from side to side, and the variation from skin to skin. A perusal of the data in the four tables will show that there is great variation in strength characteristics in some of the skins when comparing respective positions on each side of the backbone.

TABLE I

Goatskin Leathers

Tensile Strength Lbs./Sq. in.

Position Symmetry Skin	A		B		C		D		E		F	
	Left	Right	Left	Right	Left	Right	Left	Right	Left	Right	Left	Right
1	3630	2970	3386	2424	3232	3183	3172	3040	2898	2825	3162	2515
2	3197	2640	2833	2077	2168	1778	1918	1838	2309	2150	2445	2220
3	2844	2616	2719	2000	2522	2250	2347	2240	2347	2479	2415	2168
4	2769	2668	2370	2592	2558	2240	2153	2083	2240	1840	2320	2400
5	2500	2962	2443	2740	2536	2519	2461	2590	2308	2693	2295	2847
6	2260	2380	2345	2260	2000	2260	2260	2193	2250	2000	2073	2399
7	2665	2332	2639	2583	2539	2460	2383	2538	2297	2309	2139	2140
8	2332	2435	2174	2083	2000	1833	1913	1738	1918	1735	2000	1680
9	3410	3615	3460	3040	2888	2889	3070	2570	2600	2500	2600	1735
10	1693	1786	1839	1840	1691	1845	1760	1555	1778	1847	2000	2000
11	2080	2080	2000	1997	2000	1920	1925	1837	2080	1680	2000	1920
12	2460	2928	2070	2360	2000	1865	2000	1935	2260	1880	2310	1765
13	2720	3080	2595	2920	2740	2615	2500	2355	2345	2065	2965	2320
14	1540	2000	1835	1760	1750	1680	1760	1250	1855	1680	1920	1540
15	1725	1930	1785	1865	1790	1725	1870	1690	1940	1770	1430	1500
16	2415	2750	2540	2485	2300	2170	2420	2080	2415	2480	2480	1920
Average	2515	2573	2440	2314	2295	2202	2245	2096	2240	2121	2285	2067

TABLE II

Goatskin Leathers

Stitch Tear Strength Lbs./Sq. in.

Position Symmetry Skin	A		B		C		D		E		F	
	Left	Right	Left	Right	Left	Right	Left	Right	Left	Right	Left	Right
1	924	840	731	880	920	826	850	906	834	852	926	839
2	783	625	729	646	565	583	522	542	708	520	620	592
3	750	704	826	687	619	652	617	655	568	636	619	568
4	577	615	577	711	580	615	560	687	600	680	640	680
5	667	740	704	758	778	741	741	778	667	731	815	760
6	546	773	659	625	652	727	636	572	568	500	600	520
7	652	652	666	771	708	760	750	750	815	673	685	722
8	546	652	587	562	523	500	455	478	455	543	478	500
9	750	880	750	904	692	759	661	714	810	839	828	707
10	481	481	500	577	520	577	560	593	540	518	580	536
11	520	556	593	520	593	576	593	576	593	576	586	519
12	483	500	571	517	566	500	596	500	636	500	636	500
13	640	720	642	685	741	704	660	668	569	689	552	638
14	560	458	624	458	583	458	541	417	560	460	558	500
15	321	500	321	567	345	565	417	578	454	574	441	343
16	520	604	556	620	572	538	500	480	540	538	577	519
Average	608	644	627	655	622	630	604	618	620	614	634	590

TABLE III

Goatskin Leathers

Tongue Tear Strength Lbs./Sq. in.

Position Symmetry Skin	A		B		C		D		E		F	
	Left	Right	Left	Right	Left	Right	Left	Right	Left	Right	Left	Right
1	222	185	241	220	222	197	242	214	242	250	250	283
2	160	160	188	173	167	173	146	192	180	135	180	185
3	160	130	196	125	218	159	152	114	109	125	136	91
4	160	173	212	135	115	185	192	140	173	146	192	120
5	148	167	197	155	204	214	232	143	222	148	207	192
6	87	71	167	83	167	125	109	44	152	65	100	80
7	167	152	140	146	192	154	222	148	167	144	143	167
8	114	125	167	146	131	146	131	146	131	140	152	104
9	250	212	207	222	241	222	232	241	258	197	194	217
10	150	148	93	136	185	115	173	173	135	148	173	161
11	104	108	104	120	107	106	141	118	154	139	141	104
12	72	110	78	97	102	85	119	89	89	117	109	83
13	110	100	102	102	106	90	127	111	115	123	133	108
14	94	135	80	94	94	92	113	131	108	98	111	94
15	83	120	108	108	121	89	137	114	132	116	117	116
16	94	120	100	96	93	87	110	111	109	115	121	125
Average	136	138	149	135	154	140	161	139	155	138	154	139

TABLE IV

Goatskin Leathers

Ball Burst Strength Lbs. at Break

Position Symmetry Skin	A		B		C		D		E		F	
	Left	Right	Left	Right	Left	Right	Left	Right	Left	Right	Left	Right
1	70	70	68	70	65	65	60	60	60	70	70	80
2	45	45	50	55	45	43	45	55	50	40	55	60
3	55	50	45	45	45	50	47	55	50	55	57	50
4	50	50	45	45	40	45	50	45	45	55	60	60
5	55	50	57	60	50	50	50	50	54	60	55	60
6	60	60	50	45	37	35	45	35	52	55	70	60
7	55	55	50	55	52	45	55	50	45	65	60	67
8	50	55	55	55	50	50	50	50	45	50	50	55
9	70	60	70	70	75	68	75	75	75	90	80	75
10	45	45	45	40	45	40	45	35	55	60	55	50
11	37	43	45	40	43	41	45	43	50	40	52	43
12	54	52	58	52	52	56	59	57	55	60	55	60
13	57	52	55	55	57	64	61	58	62	65	57	62
14	53	50	55	45	52	40	52	45	52	50	48	49
15	59	53	57	53	62	62	60	56	62	68	55	58
16	54	60	50	55	57	52	53	49	58	55	58	55
Average	54	53	53	53	52	50	53	51	54	59	59	59

A statistical analysis of the compiled data using a three factor analysis is given in Table V. The results indicate that insufficient samples were cut from each skin to establish the best sampling location on the skin.

TABLE V

Three Factor Analysis of Variance

	Degrees of Freedom	Tensile Strength	Stitch Tear	Tongue Tear	Ball Burst
Error (Mean Square)					
SY. x P x SK.	75	43,336	4,936	487	15
		F-Values			
Between Symmetry	1	14***	1.7	16***	.07
Between Position	5	17***	1.7	1.5	18***
Between Skin	15	40***	25***	44***	47***
Symmetry x Position	5	1.3	2.0	1.2	2.8*
Symmetry x Skin	15	1.0	2.5**	1.7	1.5
Position x Skin	75	1.3	1.1	1.1	2.5***

Error—Variance Due to Error and Any Possible Three Factor Interaction.
* Significant for 5 per cent Level.
** Significant for 1 per cent Level.
*** Significant for 0.1 per cent Level.

The error term for each physical property determined would indicate that the variance is approximately 10 per cent or less in each case if we assume that the interactions are not significant among the three factors selected. The between skin variation on the basis of the F-values occurs irrespective of the physical property being studied.

Stitch tear strength shows the least influence. Tongue tear strength and ball burst strength might be used upon proper design of skin sampling. However on the basis of F-values tensile strength shows entirely too much variability to be used as an indication of process changes on these goatskin leathers.

The data on the six skins where both physical tests and layer analyses were conducted is given in Table VI. Careful examination of the physical test data shows much the same pattern as occurred on the first ten skins in regards to physical properties. Examination of the grease analyses of the respective layers shows that there is not only variation from skin to skin but also variation within a skin and that the skins show no characteristic pattern as to deposition of grease in any layer. Of most interest however is the lack of relation of the grease content of the respective layers to the various strength characteristics.

TABLE VI

		Tensile Strength	Stitch Tear	Tongue Tear	Ball Burst	Total Grease %	Grease Distribution Grain %	Corium %	Flesh %
Goatskin A									
Position	Right	2080	556	108	43	9.3	7.4	7.0	13.5
A	Left	2080	520	104	37	8.9	6.3	7.4	12.4
	Right	1997	520	120	40	8.4	7.4	6.4	11.7
B	Left	2000	593	104	45	8.6	6.4	7.3	12.1
	Right	1920	576	106	41	8.2	5.7	6.8	12.1
C	Left	2000	593	107	43	8.6	6.1	7.2	12.4
	Right	1837	576	118	43	7.9	6.3	6.7	11.1
D	Left	1925	593	141	45	8.2	6.4	6.4	11.9
	Right	1680	576	139	40	8.9	7.3	7.1	12.3
E	Left	2080	593	154	50	9.2	6.9	8.0	12.7
	Right	1920	519	104	43	9.1	7.5	7.9	11.8
F	Left	2000	586	141	52	9.3	7.7	8.1	12.2
Average		1960	567	120	43	8.7	6.8	7.2	12.2
Goatskin B									
Position	Right	2928	500	110	52	6.2	4.8	4.5	9.4
A	Left	2460	483	72	54	6.0	4.8	3.2	9.5
B	Right	2360	517	97	52	5.3	5.3	3.2	8.4
	Left	2070	571	78	58	5.8	5.4	3.1	8.9
C	Right	1865	500	85	56	5.5	5.1	3.4	8.0
	Left	2000	566	102	52	5.8	4.5	3.3	9.5
D	Right	1935	500	89	57	5.1	4.9	2.5	7.9
	Left	2000	596	119	59	5.6	3.6	3.7	9.6
E	Right	1880	500	117	60	5.6	4.9	3.4	8.4
	Left	2260	636	89	55	5.4	4.7	4.0	7.5
F	Right	1765	500	83	60	4.9	4.9	2.8	7.1
	Left	2310	636	109	55	5.5	5.2	2.7	8.8
Average		2152	542	96	56	5.6	4.8	3.3	8.6
Goatskin C									
Position	Right	3080	720	100	52	4.9	4.8	3.6	6.3
A	Left	2720	640	110	57	4.8	5.5	3.6	5.4
B	Right	2920	685	102	55	5.2	5.0	3.9	6.6
	Left	2595	642	102	55	4.8	5.3	3.8	5.3
C	Right	2615	704	90	64	4.9	5.1	4.0	5.8
	Left	2740	741	106	57	4.9	5.8	3.7	5.0
D	Right	2355	668	111	58	4.9	5.3	4.0	5.3
	Left	2500	660	127	61	4.9	6.2	3.6	4.9
E	Right	2065	689	123	65	5.4	6.1	5.1	5.1
	Left	2345	569	115	62	5.1	6.4	3.6	5.3
F	Right	2320	638	108	62	5.1	6.2	4.3	4.8
	Left	2965	552	133	57	5.3	6.9	3.8	5.3
Average		2602	658	110	59	5.0	5.7	3.9	5.4

Summary

There is a significant variation from skin to skin from the standpoint of the physical properties determined. The skins do not show any characteristic pattern as to deposition of grease in any of the three layers analyzed nor

as to total grease content. Therefore the physical properties of the goatskin leathers tested do not show any relation to the grease content.

TABLE VI (Con't.)

		Tensile Strength	Stitch Tear	Tongue Tear	Ball Burst	Total Grease %	Grease Distribution Grain %	Corium %	Flesh %
Goatskin D									
Position	Right	2000	458	135	50	7.1	6.1	5.2	10.1
A	Left	1540	560	94	53	7.2	5.3	4.6	10.2
B	Right	1760	458	94	45	7.0	5.8	5.2	10.0
	Left	1835	624	80	55	6.7	5.2	4.3	10.1
C	Right	1680	458	92	40	6.8	5.7	4.8	9.9
	Left	1750	583	94	52	6.8	5.6	4.5	10.4
D	Right	1250	417	131	45	7.3	6.2	5.3	10.5
	Left	1760	541	113	52	7.5	6.1	5.4	11.0
E	Right	1680	460	98	50	7.2	5.8	5.2	10.7
	Left	1855	560	108	52	7.3	6.0	5.3	10.6
F	Right	1540	500	94	49	7.2	6.2	5.1	10.3
	Left	1920	558	111	48	7.6	7.0	5.1	10.8
Average		1714	515	104	49	7.1	5.9	5.0	10.4
Goatskin E									
Position	Right	1930	500	120	53	5.5	4.8	3.8	7.8
A	Left	1725	321	83	59	5.0	4.0	3.1	7.9
B	Right	1865	567	108	53	5.6	4.9	4.6	7.4
	Left	1785	321	108	57	5.0	4.1	3.3	7.5
C	Right	1725	565	89	62	5.4	4.8	3.5	7.9
	Left	1790	345	121	62	4.9	4.2	3.2	7.3
D	Right	1690	578	114	56	5.6	4.8	3.8	8.1
	Left	1870	417	137	60	5.1	4.3	3.3	7.5
E	Right	1770	574	116	68	5.7	5.0	4.3	7.8
	Left	1940	454	132	62	4.9	4.3	3.5	6.9
F	Right	1500	343	116	58	5.4	4.7	4.0	7.6
	Left	1430	441	117	55	5.1	4.3	3.5	7.5
Average		1752	452	113	59	5.3	4.5	3.6	7.6
Goatskin F									
Position	Right	2750	604	129	60	5.0	5.5	3.3	6.2
A	Left	2415	520	94	54	4.8	5.4	3.4	5.6
B	Right	2485	620	96	55	4.8	5.7	3.3	5.5
	Left	2540	556	100	50	4.8	5.9	3.4	5.0
C	Right	2170	538	87	52	4.9	5.9	3.3	5.5
	Left	2300	572	93	57	4.6	5.7	3.5	4.7
D	Right	2080	480	111	49	4.8	6.1	3.3	5.0
	Left	2420	500	110	53	5.2	6.6	3.8	5.1
E	Right	2480	538	115	55	5.5	6.9	4.1	5.5
	Left	2415	540	109	58	5.0	5.8	3.9	5.2
F	Right	1920	519	125	55	5.4	6.9	3.9	5.3
	Left	2480	577	121	58	5.3	6.5	3.9	5.5
Average		2371	547	107	55	5.0	6.1	3.6	5.3

Bibliography

1. McLaughlin, G. D., and Theis, E. R., "The Chemistry of Leather Manufacture" Reinhold Publishing Co., New York. (1945).

2. Koppenhoefer, R. M., *J.A.L.C.A.* **40,** 277 (1945).
3. Roddy, W. T., Brown, J. B., and O'Flaherty, F. *J.A.L.C.A.* **45,** 72 (1950).
4. Cox, W. R., and Roddy, W. T., *J.A.L.C.A.* **45,** 270 (1950).
5. Roll, B., *J.A.L.C.A.* **47,** 40 (1952).
6. Pankhurst, K. G. A., Mitton, R. G., Innes R. F., and Johnson R. N., *J.S.L.T.C.* **36,** 379 (1952).
7. Shuttleworth, S. G., *J.S.L.T.C.* **37,** 2 (1953).
8. Koppenhoefer, R. M., *J.A.L.C.A.* **47,** 280 (1952).
9. Koppenhoefer, R. M., and Retzsch, C. E., *J.A.L.C.A.* **35,** 78 (1940).
10. American Leather Chemists Association Methods of Sampling and Analysis (1947).
11. Vickers, R. A., *J.A.L.C.A.* **46,** 417 (1951).
12. Brownlee, K. A., "Industrial Experimentation", Chemical Publishing Co., Inc., (1949).

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ABSTRACTS

The Modern Coordination Concept as a Theoretical Basis of the Tanning Process. By A. Küntzel. *Das Leder* **3,** 196 (1952). A review of Werner's coordination theory and Stiasny's application of it to tanning agents and reactions. Werner developed his theory from a study of solid, crystalline complex salts. Tanning is concerned with metal complexes in aqueous solution. The metal salts are mixtures of different salt types in complex, complicated equilibria. The individual components can be obtained in crystalline form only in exceptional cases. The investigation of these equilibria presents far greater difficulty than the analysis of simple crystalline salts. I. D. C.

New Investigations on Fur Dressing and Fur Improvement. By F. Stather. *Das Leder* **4,** 9 (1953). A review of work on furs at the Leather Institute, Freiberg, Germany. Fur skins are quite similar to skins used for making leather with the exceptions that fur skins contain more fat (20-51%) and the hairs grow from collective follicles, containing from 4-30 hairs. Dressing by the Leipzig pickles method is not satisfactory; the tannage is reversible and in damp weather the fur may deteriorate in as short a time as 3 months. Pickling fur skins is important as a replacement for liming. Formaldehyde, either alone or in combination, gives a stable tannage. Chrome tannage is satisfactory, if the Cr_2O_3 content is not too high and neutralization is not carried too far. Killing the fur with alkali removes the medulla from the hairs, leaving hollow, bleached tubes. It may also reduce dyeing of the medulla. I. D. C.

The Fundamental Properties of Dyestuffs. By Gerhard Otto. *Das Leder* **4,** 1 (1953). All who dye chrome leather know, that many dyes contain a small amount of a component that penetrates to the interior of the leather and dyes it yellow. This component has less affinity for leather than those fixed on the leather surface. Black and dark blue dyes have great affinity for chrome leather, and, if used in small amounts, dye only the surface. Dyeing is a property possessed only by compounds with double bonds. The two electron pairs in the double bond are not the same. One pair (the σ pair) is firmly bound; the other (π electrons) is only loosely bound. The latter, the π electrons, may strengthen or weaken the σ electron bond. They may be symmetrically or unsymmetrically distributed in the atom and give rise to mesomers. The benzene ring has 5 mesomers. Only

if there are unstable and fleeting mesomers in a compound, does it have ability to dye. A molecule with only a few mesomers absorbs in the ultraviolet. Substitution in the benzene ring, e.g., a nitro group, changes the absorption to violet and the dye is therefore yellow. More mesomerism is necessary to produce red, green, blue or black dyes, therefore a large molecule with added groups to give solubility is required. But recent work has shown, that this heteropolarity required for color is also the change that is needed to increase the affinity of the dye for animal or vegetable fibers. Only weak polar valence forces are involved, as is shown by the fact that the dyes act with vegetable fibers which have no salt forming groups. Secondary valence forces are found where dipoles are active between the two reacting substances. Hydrogen bonds are also involved. Ionic forces are important because, if the pH value is such that ionization occurs, there will be a tendency toward neutralization. The electrostatic force will draw the dye and fiber together. If many electrovalent groups are present in the dye, it will approach the hide fiber only to the range of the polar forces. If, however, one or only a few electrovalent groups are present, the dye will reach the range of the nonpolar forces and coordinate bonds will form. Ionic bonds hydrolize easily; they interfere with formation of coordinate bonds and therefre with tanning. Take-up of dye by polyamid fibers, and also by collagen, decreased as the number of sulfo groups in the dye increased. Nonionic dyes as well as anionic dyes were taken up in greater amount by chrome leather than by untanned hide substance; this indicates that the additional combination with the metal atom of the tanning material is of a coordinate nature. I. D. C.

The Possibility of Using Ultrasonics in the Tannery. By F. Witke. *Oesterreichische Leder-Zeitung* **8,** 26 (1953). Possible uses for ultrasonics in tanning are pointed out with the object of encouraging investigations in this field. I. D. C.

How to Organize a Fight Against the Warble Fly. By N. Fiolic. *Koza i Obuca* (*Leather and Shoes*), **2,** 53 (1953). The warble fly is causing an annual loss of more than 300 million dinars because about 30 percent of all the cattle hides in Jugoslavia show warble damage. It is suggested that collaborative effort to eradicate the pest be carried on between the leather industry, hide dealers, dairying companies, breeding cooperatives and veterinary services.

Regeneration of Chrome from Spent Tan Liquors. By E. Ludviger. *Koza i Obuca* **2,** 61 (1953). Directions are given for the erection of a regeneration plant. The process is described and the economies to be effected by its adoption are stressed.

Conference on Colonial Hides and Skins. Summarized Report of the Proceedings. *Colonial Plant and Animal Products*, **3,** 83 (1952-1953). Colonial hides and skins are a valuable article of commerce with exports advancing to 13.5 million pounds in 1951; hence the desirability of a conference to discuss the subject. The agenda covered the following subjects: drying of hides and skins, flaying and after-cleaning, dry salting of skins, buying systems, grading and marking, port inspection, export cess, hide improvement services, instruction by films, branding, damage from various sources, cracking, and baling. Papers were read on the foregoing subjects in the order named by J. R. Furlong, A. E. Knew, H. Phillips, M. H. French, J. R. Furlong, M. H. French, J. T. H. Pettit, R. J. Simmons, D. E. Faulkner, J. B. Solomon, R. Withinshaw, J. T. H. Pettit and M. H. French. Each paper was followed by discussions. The conference report covers the status of colonial hide and skin situation in a very thorough manner.

Leather Soles Are Supreme for Comfort. By H. Phillips. *Lea. World* **45.** 257 (1953). In spite of competitive synthetic products, leather remains the best material for shoe soles. This claim is based on its superior insulating qualities, its greater capacity to absorb perspiration, its better thermostatic properties, and its lesser tendency to undergo dimensional change. These factors spell greater foot comfort and better retention of shoe shape.

Resins from Sulfited Tannins as Adhesives for Wood. By L. K. Dalton. *Australian J. Applied Sci.* **4,** 136 (1953). Tannin solutions after heating with sulfites had low viscosities and are suitable for the preparation of adhesives to be spread by mechanical rolls. The conditions for treatment with sulfite were determined for extracts from Eucalyptus crebra F.u.M. and Pinus radiata D.Don and for commercial mimosa extract. The sulfited tannin solutions, mixed with paraformaldehyde and a filler, were examined as adhesives for plywood. Strong, water resistant bonds were obtained with all three adhesives.

How Does Industry Make a Pollution and Waste Survey. By J. E. Cooper. *Water and Sew. Works* **100.** 229 (1953). Analytical data comparing results obtained on water The major components are listed as (a) the plant study; (b) measurement of waste flows; (c) analysis of samples of the waste flow; and (d) report of findings. The considerations that need to be taken into account when a survey is to be undertaken are discussed in detail. The need of a liberal "getting ready period" is emphasized, as well as the necessity of full cooperation from all plant supervisors. J.F.W.

Methyl Purple vs. Methyl Orange in Alkalinity Titrations. By R. W. Frey. *Water and Sew Works* **100,** 229 (1953). Analytical data comparing results obtained on water and sewage samples titrated for alkalinity using methyl purple and methyl orange are presented which indicate that the two indicators give comparable results. The end-point carried to a distinct purple with methyl purple is sharp and in the author's opinion far superior to methyl orange J.F.W.

Theory and Practice in Stream Pollution Control. By R. D. Hoak. *The Scientific Monthly* **75,** 166 (1952). There are two principal reasons for the difficulty often experienced in gaining full agreement on pollution control measures. The first, and more important, is our meager knowledge of the specific effects of most pollutants on stream ecology and water usage. The second is the large part usually played by subjective judgment in deciding on control methods. The paramount objective of all pollution control measures should be to maintain those stream conditions that will best serve the over-all interests of particular localities. It is economically unrealistic to expect streams in highly industrialized areas to be in as good condition as those flowing through agricultural or forest land. On the other hand, gross pollution is an offense to human decency, and such conditions should be corrected by appropriate controls. It is becoming increasingly important to recognize that streams constitute a basic part of every waste treatment plant. The problem of the engineer is to recommend that degree of waste treatment which will utilize the self-purification capacity of the receiving water to the fullest practical extent consistent with optimum local conditions. Pollution of streams occurs when any material is present in such quantity that the natural balance is disturbed to the extent that desirable aquatic life is destroyed or

driven away. Streams can be said to be polluted only when the kind or amount of substances discharged to them is continually greater than a reasonable fraction of their capacity for self purification. The availability of dissolved oxygen is the most important factor in the natural purification of streams. The importance and need for comprehensive stream surveys to determine their self-purification capacity and water quality criteria is emphasized. The author discusses in some detail the pros and cons of the various control measures now in force such as, the setting of limitations on the physical, chemical and biological characteristics of the wastes, and some of those being advocated, such as biological indices of the receiving streams. There is a growing conviction that streams themselves must provide the final criteria of what may be discharged to them. This attitude reflects an acknowledgement of the economic importance of streams as an agency for assimilation of the wastes of civilization. At the same time, it recognizes the rights of downstream riparian owners, the capacity of streams for self-purification, and the aesthetic and recreational values of undefiled bodies of natural water. J.F.W.

A Single Dilution Technique for B.O.D. Studies. By H. E. Orford and I. Gellman. *Sew. and Ind. Wastes* **25,** 284 (1953) The method consists of filling two 1-gallon jugs with the diluted mixture to be studied. The first jug is kept completely full and stoppered. Samples for dissolved oxygen and any other desired analyses are siphoned from the first jug and replaced from the second jug after sampling so that the first jug is kept completely full and reaeration is prevented. When the dissolved oxygen content of the jugs is near depletion, the contents are reaerated and the process continued. The advantages of the method are: 1. All B.O.D. measurements are made on one diluted sample. 2. Additional portions can be taken from the same diluted sample for other tests. 3. Smoother, more easily analyzed B.O.D. curves are obtained than with the standard bottle dilution method. 4. Less incubator space is required because long-range B.O.D. studies can be made with only two 1-gallon jugs instead of a larger number of individual B.O.D. Bottles. J.F.W.

A Critical Review of the Literature of 1952 on Sewage Waste Treatment and Water Pollution. By H. Heukelekian, et al. *Sew. and Ind. Wastes* **25,** 511 and 633 (1953). A comprehensive review of the 1952 literature is presented under the following headings: Analytical Methods, 55 references; Sewage, 129 references; Radioactivity, 51 references; Industrial Wastes, 149 references (5 tannery waste); Water Pollution, 250 references. A general summary is given and significant trends noted.

Anaerobic Digestion of Packing Plant Wastes. By W. J. Fullen. *Sew. and Ind. Wastes* **25,** 576 (1953). Anaerobic treatment of packinghouse wastes has been under investigation by George A. Hormel & Co. for the past 3½ years. The initial laboratory work was done in 55 gal. oil drums and promising enough results obtained after one year to warrant larger-scale investigations. Work on the pilot-plant unit was started in July, 1950. Basicly the process consists of mixing in a digester the incoming raw waste with an activated anaerobic sludge at a temperature of 92-94 F., and then effecting a separation of sludge from the mixture and returning it to the digester. The author includes a comprehensive description of the operations and summarizes as follows: 1. Packinghouse wastes seem to be peculiarly adopted to anaerobic digestion, because thermal and mineral requirements are intrinsically present. 2. Wastes of a wide range of concentration can be di-

gisted with a detention time of 24 hr. or less. 3. B.O.D. removals of 95 to 96 percent can be obtained. 4. Volatile solids loadings of the digester from 0.061 to 0.081 lb. per cu. ft. per day have been demonstrated. 5. B.O.D. Loadings of the digester ranging from 0.067 to 0.084 lb. per cu. ft. per day have been recorded. 6. A practical method of continuously removing entrained gas from the digester by vacuum is described. 7. An optimum ratio of culture to substrate has not been demonstrated. 8. The maximum B.O.D. loading of the digester has not been established. 9. The anaerobic effluent is amenable to further aerobic treatment, if necessary 10. A nominal amount of sludge will be produced for disposal. 11. The anaerobic method seems to offer economic advantages, both in construction and operating costs. 12. The anaerobic method lends itself to compactness of design.

J.F.W

Synthesis and Properties of Synthetic Oiling Materials. By Richard Gutensohn. *Das Leder* **4,** 30 (1953). The preparation of synthetic leather oils and liquors during the war is reviewed. The starting material was Kogasin, a fraction of the product of the Fischer-Tropsch process of making paraffin hydrocarbons. Mepasin was made by hydrogenating Kogasin to remove unsaturation. The Derminols were made by chlorinating Kogasin. Mersol was Mepasin-sulfochloride ($C_{16}H_{33}SO_2Cl$), Derminol I was made up principally of chlorokogasin. mepasinsulfamid ($C_{16}H_{33}SO_2NH_2$) and Mepasinsulfamidoacetic acid ($C_{16}H_{33}SO_2NHCH_2COOH$). The water insoluble synthetic oils were used as substitutes for fish oil, tallow or degras. Both the water insoluble and the water emulsifiable materials have certain advantages over natural fats and oils. They are usually clearer, less liable to spue, are stable to light, oxidation and bacterial or mold action. They have uniform physical properties whereas the properties of natural oils vary greatly. For example the acid numbers of various fish oils range from 1 to 127 and the viscosity from 4.8 to 12.0 (Engler). The water soluble materials give very fine dispersions that are more stable to chemicals than sulfated natural oils. The fat take up by leather is more uniform but the leather is drier. By suitable alteration of the proportions and kinds of oils and emulsifiers, however, the oiling requirements of all kinds of leathers from dry, supple to firm, greasy leather can be met. Illustrations are given to show the separation in 24 hours of a surface layer from a 10-fold. sulfated fish oil emulsion and in 1 hour from an emulsion of 7 grams sulfated fish oil and 3 grams neatsfoot oil (in 100 ml.). When half of the fish oil was replaced by Derminollicker as. very stable emulsions were formed with particle size of less than one micron.

I.D.C.

The Problem of the Retannage of Rapid-Tanned Sole Leather. By Karl Blach. *Oesterreichische Leder-Zeitung* **8,** 4 (1953). By proper retannage, rapid tanned sole leather may be greatly improved and made equal or superior to slow tanned sole leather. Retannage increases combined tannin, degree of tannage, yield, and water resistance. For retannage, Hausruck extract, a sulfite cellulose preparation, is cheaper than quebracho. I.D.C.

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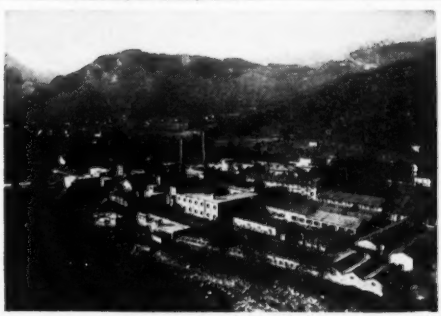

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THE TANNER'S COUNCIL RESEARCH LABORATORY
Universtty of Cincinnati

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CORN SYRUP
CORN STARCH
LACTIC ACID
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Binder and Filler

PIGMENT FINISHES Uniform quality binder, filler and carrying agent. Builds up body. Improves covering power and spread. Nourishes fiber and eliminates harsh feel. No manipulation necessary.

LEATHER FILLER Imparts permanent flexibility. Does not "pipe" or crack. Covers cuts and imperfections.

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TYPICAL A.L.C.A. ANALYSIS

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NON-TANNIN	21.65	21.2	19.1
INSOLUBLES	.65	.6	.7
WATER	15.98	11.5	6.7
ASH	.67	.82	.75

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HIGHEST QUALITY—MADE UNDER THE SUPERVISION
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SOLE AGENTS

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A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

TANNIN	61.55
NON-TANNIN	16.03
INSOLUBLES	1.70
WATER	20.72

Also Available as Liquid with 30% Tannin

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tannages, it has given better yields and improved color.

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